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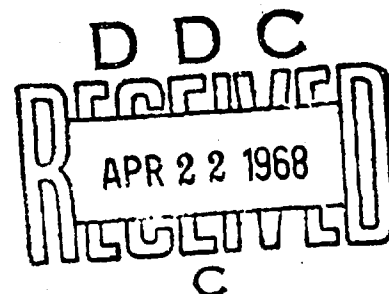
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## ENGINEERING DESIGN HANDBOOK

## MILITARY PYROTECHNICS SERIES

PART THREE—PROPERTIES OF MATERIALS USED  
IN PYROTECHNIC COMPOSITIONS

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## PREFACE

This handbook constitutes Part Three of a planned series on Military Pyrotechnics and forms part of the Engineering Design Handbook Series of the Army Materiel Command. Part Three is devoted to the presentation of data on the principal ingredients of pyrotechnic compositions. The information is presented on data sheets, representing a total of 123 ingredients. The data presented here have been collected from many sources and are intended to facilitate reference and the making of calculations by chemical engineers and physicists in the field of pyrotechnics. A single reference list, showing the main sources of data, is included and each reference is keyed in by number to appropriate entries on the data sheets. References that pertain only to a specific data sheet are listed at the end of the data sheet under Additional References.

Part Two, a separate handbook with the same date of publication, deals with the problems of safety in the pyrotechnics laboratory and plant, processing procedures and equipment, particle size procedures, and contains a glossary of terms.

Part One, under preparation at the time of publication of Parts Two and Three, will deal with the physical and chemical theoretical aspects of the production of pyrotechnic effects, and the application of the theory to practice. It will also include a history of the pyrotechnic art and an extensive bibliography.

A future volume, currently in the planning stage, will be devoted to discussion of methods used in the evaluation of pyrotechnic items, determination of their compliance with the requirements of the using services, special equipment and procedures which are followed in tests and evaluation, and considerations affecting the interpretation of results.

Material for Parts Two and Three was prepared by McGraw-Hill Book Company for the Engineering Handbook Office of Duke University, prime contractor to the Army Research Office--Durham. The entire project was under the technical guidance of an interservice committee, with representation from the Army Chemical Center, Ballistics Research Laboratories, Frankford Arsenal, Harry Diamond Laboratories, Picatinny Arsenal, U. S. Naval Ammunition Depot (Crane), U. S. Naval Ordnance Laboratory, and U. S. Naval Ordnance Test Station. Chairman of this committee was Mr. Garry Weingarten of Picatinny Arsenal.

Agencies of the Department of Defense, having need for Handbooks, may submit requisitions or official requests directly to Equipment Manual Field Office (7), Letterkenny Army Depot, Chambersburg, Pennsylvania. Contractors should submit such requisitions or requests to their contracting officers.

Comments and suggestions on this handbook are welcome and should be addressed to Army Research Office--Durham, Box CM, Duke Station, Durham, North Carolina 27706.

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# ABBREVIATIONS AND SYMBOLS\*

A.	Angström unit(s)
<u>a</u>	length of side (X-ray data) in Angström units
abs.	absolute
Acta Chem. Scand.	Acta Chemica Scandinavica (Copenhagen, Denmark)
Acta Cryst.	Acta Crystallographica
addnl.	additional
alc.	alcohol
alk.	alkaline
amor.	amorphous
Anal. Chem.	Analytical Chemistry
Anal. Chim. Acta	Analytica Chimica Acta
Ann. Physik	Annalen der Physik
app.	apparatus
approx.	approximate(ly)
A. S. T. M.	American Society for Testing Materials
at.	atomic
av.	average
atm.	atmosphere(s), atmospheric
<u>b</u>	length of side (X-ray data) in Angström units
Ber.	Berichte der deutschen Chemischen Gesellschaft
B. M.	Bureau of Mines, Dept. of the Interior
B. P.	black powder
b. p.	boiling point

\*Abbreviations and symbols in the following data sheets generally correspond to those in Chemical Abstracts.

Br. Chem. Abstr.	British Chemical Abstracts
Bull. Am. Ceram. Soc.	Bulletin of the American Ceramic Society
c	crystal(s)
<u>c</u>	length of side (X-ray data) in Angström units
C.A.	Chemical Abstracts
cal.	calories(s)
Can. J. Technol.	Canadian Journal of Technology
cc.	cubic centimeter(s)
Chem. Eng. News	Chemical and Engineering News
c. f. m.	cubic feet per minute
Chem. Eng. Prog.	Chemical Engineering Progress
C. I.	Colour Index (refs. 48 and 48A)
Chem. Revs	Chemical Reviews
coefficient	coefficient
composn. (s)	compositions
Compt. rend.	Compte rendus hebdomadaires des Séances de l'Académie des Sciences, Paris, France
concd.	concentrated
concn.	concentration
C. P.	chemically pure
cryst.	crystalline
cu. ft.	cubic foot
d.	density
DDTA	derivative differential thermal analysis
decomp.	decomposes
dil.	dilute
diln.	dilution

DTA	differential thermal analysis
equil.	equilibrium
equiv.	equivalent
est.	estimate
estd.	estimated
f. p. m.	feet per minute
g.	gram(s)
HC	Hexachloroethane Smoke Mixture
HL	high explosive
ICC	Interstate Commerce Commission
I. C. T.	International Critical Tables (Ref. 42)
Ind. Eng. Chem.	Industrial Engineering Chemistry
insol.	insoluble
i. v.	intravenously
J. Am. Chem. Soc.	Journal of the American Chemical Society
J. Am. Ceram. Soc.	Journal of the American Ceramic Society
J. Appl. Polymer. Sci.	Journal of Applied Polymer Science
J. Chem. Phys.	Journal of Chemical Physics
J. Chem. Soc.	Journal of the Chemical Society (London)
J. Colloid Sci.	Journal of Colloid Science
J. Electrochem. Soc.	Journal of the Electrochemical Society
J. Franklin Inst.	Journal of the Franklin Institute (Philadelphia)
J. Phys. Chem.	Journal of Physical Chemistry
J. Research NBS	Journal of Research of the National Bureau of Standards
J. Soc. Dyers Colourists	Journal of the Society of Dyers and Colourists
k-	kilo
Kcal.	Kilocalorie

kg.	kilogram
l	liquid
l.	liter(s)
L. D.	lethal dose
liq.	liquid
m., m. <sup>3</sup>	meter, cubic meter
M. A. C.	Maximum Allowable Concentration (based on continuous exposure for an 8-hr. day)
manuf. (g)	manufacture, manufacturing
M. C. A.	Manufacturing Chemists Association
Mém. artillerie franç.	Mémorial de l'artillerie française (Paris)
Mém. poudres	Mémorial des Poudres (Paris)
mg.	milligram(s)
min.	minimum
M. L. D.	minimum lethal dose
mm.	millimeter
mol.	molecular
m. p.	melting point
NG	nitroglycerine
OSM	Ordnance Safety Manual
P. A.	Picatinny Arsenal
PATR	Picatinny Arsenal Technical Report
pdr.	powder
powd.	powdered
p. p. m.	parts per million
press.	pressure
Proc. Roy. Soc.	Proceedings of the Royal Society (London)

psi	pounds per square inch
pt	part
Pyro	pyrotechnics
Rec. trav. chim.	Recueil des Travaux Chimiques des Pays-Bas (Dordrecht, Netherlands)
Rev.	revision
R. H.	relative humidity
rhbdr.	rhombohedral
rhomb.	rhombic, orthorhombic
R. I.	report of investigation (followed by number)
R. T.	room temperature
satd. soln.	saturated solution (hygroscopicity determinations)
S	System (used with Ref. 44)
sl.	slightly
sol.	soluble
soly.	solubility
spec.	specification
sp. gr.	specific gravity
S. P. I.	Society of Plastic Industries
stat	static
S. T. P.	Standard Temperature and Pressure
sup	supplement
T	temperature
tech.	technical(ly)
temp.	temperature
TGA	thermogravimetric analysis
Trans. Faraday Soc.	Transactions of the Faraday Society (Aberdeen, Scotland)

T. P.	transition point
U. L.	Underwriters Laboratories, Inc., Bulletin of Research
U. N.	United Nations
vac.	vacuum
vol., V.	volume
wt.	weight
Zeit. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie
Z. Elektrochem.	Zeitschrift für Elektrochemie und angewandte physikalische Chemie (Berlin)
Zeit. Physik.	Zeitschrift für Physik
Zhur. Fiz. Khim.	Zhurnal Fizicheskoi Khimii (Journal of Physical Chemistry, Moscow, U. S. S. R.)

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\*This listing gives the main sources from which material has been collected. Numbers in the Ref. column on each data sheet are keyed to these general references.

References that pertain only to specific data sheets are listed at the end of the data sheets under Additional References. Numbers in the Ref. column preceded by Addnl. Ref. are keyed to those references. Some Additional References are sources from which no data were taken but which contain pertinent information on specific ingredients.



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- 91) Chemical Engineers' Handbook, R. H. Perry et al., Eds., McGraw-Hill Book Company, Inc., New York (1950)
- 92) "Toxicity of Nine Dyes. A Literature Study," N. Anson and P. Parent, C. W. L. Tech. Memo. 47-6, Toxicological Information Center, Army Medical Center, Md. (1959)
- 93) "Toxic Hazards Associated with Pyrotechnic Items," Ordnance Pamphlet 2793, U.S. Naval Ordnance Laboratory (1957)
- 94) Rare Metals Handbook, 1st ed., C. A. Hampel, Reinhold Publishing Corp., New York (1956); 94A) 2nd ed. (1961)
- 95) Engineering Materials Handbook, C. L. Mantell, Ed., McGraw-Hill Book Company, Inc., New York (1958)
- 96) Crystal Data, J. D. H. Donnay and W. Nawacki, Geological Society of America, New York (1954)
- 97) "Standard X-Ray Diffraction Powder Patterns," National Bureau of Standards Circular 539 (1953-60)

**ACETONE, (CH<sub>3</sub>)<sub>2</sub>CO**  
(Dimethyl Ketone, β-Ketopropane, 2-Propanone, Pyroacetic Ether)

Structural Formula:	$\text{H}_3\text{C}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_3$
Specification No.:	JAN-A-489
Molecular Weight:	58.08
Crystalline Form:	liquid
Color:	colorless
Density, g./ml.:	(liquid) 0.792 at 4-20°C
Coefficient of Thermal Expansion, cubical at 20°C:	$1.487 \times 10^{-3}$
cubical at 0-54°C:	$V_t = V_0 (1 + 1.3240t^{-3} + 3.8090t^{-6} - 0.87983t^{-9})$
Heat of Formation, Kcal./mole at 298°K:	(liquid) -59,240
Free Energy of Formation, Kcal./mole at 298°K:	-37,120
Entropy, cal./deg./mole at 298°K:	47.9
at B.P. (ideal gas):	72.7
Melting Point:	177.5°K (-95.5°C)
Heat of Fusion, cal.(15°)/g.:	23.4
Boiling Point:	329.5°K (56.5°C)
Heat of Vaporization, cal./g. at 56.1°C:	124.5
cal./mole:	6952 ± 1
Transition Point:	—
Heat of Combustion, Kcal./mole at 20°C and 1 atm.:	426.8
Heat of Sublimation:	—
Autoignition Temperature, in air:	700°C 1113°F
Enthalpy Change of Enolization at 25°C:	
Me <sub>2</sub> CO (liquid) → CH <sub>2</sub> =CMeOH (liquid) Kcal./mole:	

**HEAT CAPACITY OF ACETONE**  
Set I, Reverse-flow Calorimeter, 760 mm.

t, °C	61	75	90	105
T, °K	334	348	363	378
c <sub>p</sub> , cal./g./deg.	0.375	0.374	0.380	0.384
C <sub>p</sub> , cal./mole/deg.	21.8	21.7	22.1	22.3
t, °C	120	135	155	165
T, °K	393	408	428	438
c <sub>p</sub> , cal./g./deg.	0.390	0.398	0.416	0.420
C <sub>p</sub> , cal./mole/deg.	22.7	23.1	24.2	24.4

**Refs.**

- 1  
1  
Addnl. Ref. 4  
Addnl. Ref. 5  
Addnl. Ref. 5  
Addnl. Ref. 6  
1  
1  
1  
1, 42  
Addnl. Ref. 7  
1  
71  
75  
Addnl. Ref. 2  
7  
Addnl. Ref. 1

Acetone, (CH<sub>3</sub>)<sub>2</sub>CO (page 2)

Set II, Direct-flow Calorimeter, 760 mm.

t, °C	59.4	74.6	99.1	149.4
T, °K	332.6	347.8	372.3	422.6
c <sub>p</sub> , cal./g./deg.	0.376	0.374	0.380	0.406
C <sub>p</sub> , cal./mole/deg.	21.8	21.7	22.0	23.6

See also Addnl. Ref. 8

Decomposition Temperature and Products: Between 506° and 632°C, the products of decomposition are about 1/2 saturated hydrocarbons and hydrogen, 1/3 CO, and the remainder CO<sub>2</sub> and ethylene.

52V1,  
Addnl. Ref. 3

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	-59.4	-31.1	-9.4	+7.7	39.5	56.5	-94.6

1

X-Ray Crystallographic Data:

Interatomic Distances and Molecular Configuration

C - C	1.57 ± 0.04A	< C - C - O	123°
C - O	1.14	Planar	
C - H	1.09		

55, 85

Hygroscopicity:

Solubility Data: Miscible in all proportions with water, alcohol, ether.  
Soluble in chloroform.

1

Health Hazard: Prolonged or repeated inhalation or contact may have a variety of harmful effects although cases of serious poisoning are rare. Also has a narcotic effect, usually not chronic.

12, 25, 29, 14

M.A.C.:

1000

Safety Classifications:

OSM: Class I, flammable liquid (flash point below 20°F)

ICC: Listed under "Explosives and Other Dangerous Articles" as a flammable liquid; red label

Underwriters' Laboratory: 90 (gasoline class)

Fire and Explosion Hazard: Dangerous when exposed to flame. The vapors form an explosive mixture with air; explosive range (% acetone by volume) 2.55 to 12.3%. Can be ignited by an electric spark. Reacts vigorously with oxidizing materials. Forms an explosive mixture with high concentrations of hydrogen peroxide. To fight fire use water, carbon dioxide, dry chemical, or carbon tetrachloride. For precautions in storage, handling, and dispensing, see Refs. 26 and 14.

12, 25, 26, 14,  
12V75

Caution: Keep away from fire.

Electrostatic Sensitivity: Readily ignited by static discharge.

14

Use in Pyrotechnics:

as a solvent

Additional References:

- 1) "The Heat Capacity of Organic Vapors. VI. Acetone," B. Collins et al., J. Am. Chem. Soc. 71, 2929 (1949)

Acetone,  $(\text{CH}_3)_2\text{CO}$  (page 3)

- 2) "The Heat of Hydrolysis of i-Propenyl Acetate and m-Cresyl Acetate and the Heat of Enolization of Acetone," S. Sunner, *Acta Chem. Scand.* **11**, 1757 (1957)
- 3) "Thermal Decomposition of Acetone in the Gaseous State," C. N. Hinshelwood and W. K. Hutchison, *Proc. Roy. Soc. A* **iii** 245 (1926). Abstracted in *Br. Chem. Abstr.*
- 4) "Free Energies of Some Organic Compounds," G. S. Parks and H. M. Hoffman, The Chemical Catalogue Co., New York (1932)
- 5) "The Heat Capacities of Isopropyl Alcohol and Acetone from 16° to 298°K and the Corresponding Entropies and Free Energies," K. K. Kelly, *J. Am. Chem. Soc.* **51**, 1145 (1929)
- 6) "The Entropy of Acetone and Isopropyl alcohol from Molecular Data. The Equilibrium in the Dehydrogenation of Isopropyl alcohol," S. C. Schumann and J. G. Aston, *J. Chem. Phys.* **6**, 485 (1938)
- 7) "The Thermodynamic Properties of Acetone," R. Pennington and K. A. Kobe, *J. Am. Chem. Soc.* **79**, 300 (1957)
- 8) "Estimation of the Heat Capacities of Organic Liquids," A. Johnson and Chen-Jung Huang, *Can. J. Technol.* **33**, 421 (1955)

**ALCOHOL, C<sub>2</sub>H<sub>5</sub>OH**  
(Ethyl Alcohol, Ethanol, Methyl Carbinol,  
Spirit of Wine, Grain Alcohol, Ethylic Alcohol,  
Rectified spirit = 90-95% alcohol)

Specification No.: MIL-E-463A  
The specification covers grades 1, 2, 5, and 6, of which only grade 2 (min. 94.9% alcohol by vol.) is used in pyrotechnics.

Molecular Weight: 46.07  
Crystalline Form: liquid  
Color: colorless  
Density, g./ml.: (liquid) 0.7893  
Coefficient of Thermal Expansion, cubical at 20°C:  $1.12 \times 10^{-3}$   
 $V_t = V_0 (1 + 1.012 \times 10^{-3} t + 2.20 \times 10^{-6} t^2)$  (for 99.3% by vol.)  
Heat of Formation, Kcal./mole at 298°K: (gas) -56.24  
(liquid) -66.356

See Table a

Free Energy of Formation, Kcal./mole at 293°K: (gas) -40.30  
(liquid) -41.77

See Table a

Entropy, Kcal./mole: (gas) 67.4  
(liquid) 38.4

See Table a

**a. ENTROPY, FREE ENERGY, AND RELATED QUANTITIES**  
**ETHYL ALCOHOL IN THE IDEAL GAS STATE AT**  
**1-ATMOSPHERE PRESSURE**  
( $E_0^\circ = -52,260$  cal./mole<sup>-1</sup>)

Refs.

1  
27  
1, 41  
9

9

9

Addnl. Ref. 5

T	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	S°	$-H^\circ$	$\Delta F^\circ$ *	$\log_{10} K$ *
°K	cal./deg. <sup>-1</sup> mole <sup>-1</sup>	cal./deg. <sup>-1</sup> mole <sup>-1</sup>	cal./mole <sup>-1</sup>	cal./mole <sup>-1</sup>	$-\Delta F^\circ / R.T.$ 2.3026
298.16	54.27	66.45	68,440	-40,010	29.329
300.00	54.34	66.56	68,560	-39,910	29.075
400	58.11	72.11	75,500	-34,310	18.749
500	61.42	77.12	82,970	-28,470	12.447
600	64.43	81.76	90,920	-22,490	8.191
700	67.22	86.08	93,310	-16,390	5.118
800	69.84	90.12	108,130	-10,230	2.796
900	72.31	93.92	117,330	-4030	0.980
1000	74.65	97.48	126,910	+2190	-0.479
1100	76.88	100.85	136,830	8430	-1.675
1200	79.02	104.04	147,080	14,630	-2.673
1300	81.07	107.06	157,650	20,920	-3.517
1400	83.03	109.94	168,500	27,170	-4.239
1500	84.92	112.67	179,640	33,410	-4.867

\*  $\Delta F^\circ$  and K are the free-energy change and equilibrium constant, respectively, for the reaction forming ethyl alcohol from its elements in their standard states at T°K.



Alcohol,  $C_2H_5OH$  (page 2)

Melting Point:	158.6°K (-114.5°C)	9
Heat of Fusion, Kcal./mole:	1.200	9
Boiling Point:	351.7°K (78.6°C)	9
Heat of Vaporization, Kcal./mole:	9.22	9
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:		

See Table b

Heat Capacity, cal./deg./mole at 298°K:	(liquid) 26.64	9
---	----------------	---

See also Addnl. Refs. 2 and 5, and Table b

b. HEAT CAPACITY AT CONSTANT PRESSURE, HEAT CONTENT, AND  
RELATED QUANTITIES OF ETHYL ALCOHOL IN THE  
IDEAL GAS STATE  
( $E_0 = -52,260$  cal./mole<sup>-1</sup>)

Addnl. Ref. 5

T	$\frac{H^\circ - E_0}{T}$	$H^\circ$	$\Delta H^\circ$ *	$C_p^\circ$
°K	cal./deg. <sup>-1</sup> mole <sup>-1</sup>	cal./mole <sup>-1</sup>	cal./mole <sup>-1</sup>	cal./deg. <sup>-1</sup> mole <sup>-1</sup>
298.16 . . . .	12.18	-48,630	-56,240	17.59
300.00 . . . .	12.22	-48,600	-56,260	17.66
400 . . . . .	14.00	-46,660	-57,250	21.00
500 . . . . .	15.70	-44,410	-58,110	24.09
600 . . . . .	17.33	-41,860	-58,780	26.81
700 . . . . .	18.86	-39,060	-59,320	29.18
800 . . . . .	20.28 *	-36,030	-59,710	31.25
900 . . . . .	21.61	-32,810	-60,000	33.07
1000 . . . . .	22.83	-29,430	-60,200	34.66
1100 . . . . .	23.97	-25,900	-60,320	36.06
1200 . . . . .	25.02	-22,240	-60,370	37.28
1300 . . . . .	25.99	-18,470	-60,350	38.34
1400 . . . . .	26.91	-14,590	-60,250	39.27
1500 . . . . .	27.75	-10,630	-60,190	40.08

\*  $\Delta H^\circ$  is the enthalpy of formation of ethyl alcohol from its elements in their standard states at the temperature T.

Decomposition Temperature: —

Decomposition Products: burns to  $CO_2$  and  $H_2O$

Alcohol, C<sub>2</sub>H<sub>5</sub>OH (page 3)

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	-31.3	-2.3	+19.0	34.9	63.5	78.4	-112

X-Ray Crystallographic Data: —

Hygroscopicity: —

Solubility Data: Miscible with water and many organic solvents in all proportions.

Health Hazard: It is not considered an industrial poison, although large doses cause nausea, vomiting, impaired perception, lack of coordination, stupor, and even death. Habitual use may cause gastritis, delirium tremens, hallucinations, peptic ulcers, and hepatic cirrhosis.

Exposure to concentrations of 5000-10,000 ppm. irritates the eyes and mucous membranes. Inhalation produces the same symptoms as ingestion.

M.A.C.: 1000

Safety Classifications:

OSM: Class I

ICC: Listed under "Explosives and Other Dangerous Articles." Flammable liquid; red label.

Fire and Explosion Hazard: Readily ignited by flame or static electric discharge. Forms explosive mixture with air.

Explosive limits in air: 3.28 to 19% alcohol by vol.

Flash point: 55°F

Autoignition temperature: 799°F (95% alc.)  
738°F (100% alc.)

For proper storage and handling see Refs.

To fight fire use CO<sub>2</sub>, dry chemical, or CCl<sub>4</sub>.

Electrostatic Sensitivity: Can be ignited by static electrical discharge.

Heat of Combustion, Kcal./mole at 20°C  
and 1 atm.: 327.6

Viscosity, centipoises at 20°C  
(for abs. alcohol): 1.22

Surface Tension, dynes/cm. at 20°C  
(for abs. alcohol): 22.5

Use in Pyrotechnics: for shellac solutions  
See Spec. JAN-S-732

Additional References:

- 1) "Thermodynamic Properties of Ethyl Alcohol," R. C. Reid and J. M. Smith, Chem. Eng. Progr. 47, 415 (1951)
- 2) "Estimation of The Heat Capacities of Organic Liquids," A. Johnson and Chen-Jung Huang, Can. J. Technol. 33, 421 (1955)

**Alcohol,  $C_2H_5OH$  (page 4)**

- 3) "Heat Capacities of  $C_{1-5}$  Aliphatic Alcohols," G. Sinko and T. DeVries, J. Am. Chem. Soc. 75, 1815 (1953)
- 4) "Ethyl Alcohol," U. S. Industrial Chemical Co., Division of National Distillers and Chemical Corp., New York (1960)
- 5) F. Brickwedde et al., J. Research NBS 57, 270 (1946)  
(thermodynamic data)
- 6) "The Technology of Solvents and Plasticizers," A. K. Doolittle, John Wiley & Sons, New York (1954)

# ALUMINUM, Al (Aluminum)

Refs.

Specification No.:

JAN-A-647

The specification covers three types, which vary in purity, and five classes, which vary in granulation and apparent density.

Type A—flat flakes manufactured by grinding or stamping.

Type B—granular or spheroidal particles manufactured by the atomizing process or by grinding.

Type C—granular or spheroidal particles manufactured by the atomizing process.

Molecular Weight: 26.98  
Crystalline Form: cubic  
Color: silvery white  
Density, g./ml.: (solid) 2.699 at 20°C  
(liquid) 2.382 at 659°C

Coefficient of Thermal Expansion:

Temp. °C	Coefficient	Temp. °C	Coefficient
-191 to +16	$18.35 \times 10^{-6}$	40	$23.14 \times 10^{-6}$
20	$25.5 \times 10^{-6}$	600	$31.50 \times 10^{-6}$

Heat of Formation, cal./mole at 298°K: (gas) 77.50

Free Energy of Formation, cal./mole at 298°K: (gas) 67.801

Entropy, cal./deg./mole at 298°K: (c) 6.769

(gas) 39.33

See Tables a, b, and c

Melting Point:  $932 \pm 1^\circ\text{K}$  (659°C)

Heat of Fusion, cal./mole: 2550

Boiling Point:  $2720^\circ\text{K}$  (2447°C)

Heat of Vaporization, cal./mole: 70,200

Transition Point: —

Heat of Transition: —

Heat of Sublimation, cal./mole at 298°K: 77,500

Heat Content or Enthalpy, cal./mole at 298.15°K: (solid) 10.94

(liquid) 7.00

(gas) 4.97

See Table a

## Aluminum, Al (page 2)

## a. HEAT CONTENT AND ENTROPY OF Al(c, l)

(Base, crystals at 298.15°K; atomic wt., 26.98)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	600	1.72	1500 . . . . .	10,830	13.59
500 . . . . .	1230	3.14	1600 . . . . .	11,530	14.04
600 . . . . .	1890	4.34	1700 . . . . .	12,230	14.46
700 . . . . .	2580	5.40	1800 . . . . .	12,930	14.86
800 . . . . .	3310	6.33	1900 . . . . .	13,630	15.24
900 . . . . .	4060	7.26	2000 . . . . .	14,330	15.60
932 (c) . . .	4280	7.50	2100 . . . . .	15,030	15.94
932 (l) . . .	4550	10.26	2200 . . . . .	15,730	16.27
1000 . . . . .	5380	10.75	2300 . . . . .	16,430	16.58
1100 . . . . .	6030	11.42	2400 . . . . .	17,130	16.88
1200 . . . . .	6730	12.03	2500 . . . . .	17,830	17.16
1300 . . . . .	7430	12.59	2600 . . . . .	18,530	17.44
1400 . . . . .	8130	13.11	2700 . . . . .	19,230	17.70

## Al(c):

Enthalpy:  $H_T - H_{298.15} = 4.94T + 1.48 \times 10^{-5}T^2 - 1604$  (0.6 percent; 293° - 932°K)Heat Capacity:  $C_p = 4.94 + 2.96 \times 10^{-5}T$ ;  $\Delta H_{932}$  (fusion) = 2570

## Al(l):

Enthalpy:  $H_T - H_{298.15} = 7.00 + 330$  (0.1 percent; 932° - 2700°K)

b. HEAT CONTENT AND ENTROPY OF Al(g)  
(Base, ideal gas at 298.15°K; atomic wt., 26.98)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	515	1.49	1900	7995	9.27
500	1020	2.62	2000	8490	9.53
600	1520	3.53	2200	9485	10.00
700	2020	4.30	2400	10480	10.43
800	2520	4.97	2600	11475	10.83
900	3020	5.55	2800	12470	11.20
1000	3515	6.08	3000	13460	11.54
1100	4015	6.55	3500	15950	12.31
1200	4515	6.99	4000	18440	12.98
1300	5010	7.38	4500	20950	13.57
1400	5510	7.75	5000	23450	14.10
1500	6005	8.10	6000	28790	15.07
1600	6505	8.42	7000	34640	15.97
1700	7000	8.72	8000	41440	16.87
1800	7500	9.00			

Al(g):

Enthalpy:  $H_T - H_{298.15} = 4.97T - 0.12 \times 10^{-5}T^2 - 1442$  (0.1 percent; 298° - 5000°K)Heat Capacity:  $C_p = 4.97 + 0.12 \times 10^{-5}T^2$ 

## c. HEAT CAPACITY OF ALUMINUM\*

5

Solid from 298° to 932°K

Liquid from 932° to 2720°K

Gas from 2720° to 3000°K

T, °K	$C_p$ (cal./deg./mole)
298	5.82
400	6.12
600	6.72
800	7.31
1000-2700	7.00
2800-3000	4.97

\*See also  $C_p$  equations directly above

Decomposition Temperature: —

Decomposition Products: —

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	1284	1487	1635	1749	1947	2056	660

1

# Aluminum, Al (page 4)

## X-Ray Crystallographic Data:

System	Space Group	a	Molecules/Unit Cell
cubic	$O_h$	5.43A	4

## Hygroscopicity, cumulative increase in weight after:

	Atomized	Stamped
Storage over $H_2O$ for 29 days:	55.2%	0.6%
Storage over $H_2SO_4$ for 29 days:	50.2%	0.0%
Two days in oven at $105^\circ C$ :	47.8%	-1.4%

## Solubility Data: In alkali; hydrochloric, sulphuric acids:

soluble  
insoluble

In nitric acid, acetic acid:

Health Hazard: None. Not usually considered an industrial poison. Aluminum dust can irritate the eyes. Inhalation of dust may cause chronic pulmonary disease.

M.A.C.:

50 million particles/ft.<sup>3</sup>  
(15 mg./m.<sup>3</sup>)

## Safety Classifications:

OSM: Class 1. Class 2 when not packed or stored in original shipping containers or equivalent (types I and II).

U.N.: Inflammable solid, which in contact with water emits flammable gas.

Fire and Explosion Hazard: Dust may ignite when exposed to heat of flame. May ignite by chemical action with oxidizers. Powder easily ignited or initiated to explosion by discharges of static electricity. See Electrostatic Sensitivity below.

Caution: Keep water away. Evolution of hydrogen gas may result in explosion. When compounded with oxidizing agents, the powdered metal is a dangerous fire and explosion hazard. Special mixtures of dry chemicals should be used to fight aluminum fires.

See also Ref. 86

Electrostatic Sensitivity: Minimum energy required for ignition of powder by electric sparks (millijoules)

	Dust Cloud	Dust Layer
Atomized:	15	2.5
Stamped:	10	1.5

Ignition Temp. of Al powders,  $^\circ C$ :

	Dust Cloud	Dust Layer
Atomized:	540	750
Stamped:	550	470

Minimum Explosive Concentration, mg./l.:

Atomized:	40
Stamped:	35

Used in Pyrotechnics: Aluminum is used as a fuel. It produces an intense white light on burning, but no distinctive flame coloration.

## Additional References:

1) Ref. 64

**ALUMINUM OXIDE,  $Al_2O_3$**   
(Alumina,  $\alpha$ -Alumina, Corundum, Alundum)

Percent Oxygen:	47.08
Specification No.:	MIL-A-10825
Molecular Weight:	101.96
Crystalline Form:	hexagonal
Color:	colorless
Density, g./ml.:	(solid) 3.99 (liquid) 2375–2625°K 5.632–1.127 $\times 10^{-4}T$

Refs.

1

1

81A

Addnl. Ref. 5

Alumina may exist in several forms at low temperature, but they are all converted to  $\alpha$ -alumina (corundum) by heating above 1600°C. The change is irreversible.

$\beta$ -Alumina is an impure form that occurs from sodium or potassium aluminate.

Form	Crystalline Structure	Density	Source	Temp. of Transformation to corundum, °C
$\alpha$	hexagonal	3.965		stable form
$\gamma$	spinel type	—	dehydration of $\gamma$ (hydrous) $Al_2O_3$	> 1200
$\gamma'$	cubic	3.619	electrolytic oxidation of Al	750–1000
$\delta$	hexagonal	2.40	dehydration of $AlCl_3 \cdot 6H_2O$	950
$\epsilon$	cubic	—	electron diffraction	—
$\zeta$	octahedron	3.6	from lithium melts	> 1600

Coefficient of Thermal Expansion, linear for alundum, 25°–900°C:  $8.7 \times 10^{-6}$

81

Heat of Formation, Kcal./mole: (corundum)  $\alpha(c)$ –399.09  
 $\gamma(c)$ –384.84

9

See Table a

Free Energy of Formation, Kcal./mole at 298°K: (corundum)–376.77

9

See Table a



Aluminum Oxide, Al<sub>2</sub>O<sub>3</sub> (page 2)

Heat and Free Energy of Formation:

a. HEAT AND FREE ENERGY OF FORMATION OF  
Al<sub>2</sub>O<sub>3</sub> (CORUNDUM)

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16 . . . .	-399,600 (± 900)	-377,800 (± 900)
400 . . . . .	-399,700	-369,600
500 . . . . .	-399,600	-362,100
600 . . . . .	-399,500	-354,600
700 . . . . .	-399,200	-347,100
800 . . . . .	-399,100	-339,700
900 . . . . .	-398,900	-332,300
931.7 . . . .	-398,800	-329,900
931.7 . . . .	-403,900	-329,900
1000 . . . . .	-403,700	-324,600
1100 . . . . .	-403,400	-316,700
1200 . . . . .	-403,000	-308,800
1300 . . . . .	-402,600	-300,900
1400 . . . . .	-402,300	-293,100
1500 . . . . .	-401,900	-285,400
1600 . . . . .	-401,500	-277,600
1700 . . . . .	-401,200	-269,900
1800 . . . . .	-400,800	-262,200
1900 . . . . .	-400,400	-254,500
2000 . . . . .	-400,100	-246,800

Phase Changes of Metal

M. P., 931.7°K; Δ H = 2570 cal./g.-atom

Energy Equations:

Reaction	Range of Validity, °K
1) 2Al(c) + 3/2 O <sub>2</sub> (g) = Al <sub>2</sub> O <sub>3</sub> (corundum)	298.16 to 931.7
$\Delta F_T^\circ = -404,480 - 15.68T \log T + 2.18 (10^{-5}T^2) + 3.935 (10^6T^{-1}) + 123.64T$	
2) 2Al(l) + 3/2 O <sub>2</sub> (g) = Al <sub>2</sub> O <sub>3</sub> (corundum)	931.7 to 2000
$\Delta F_T^\circ = -407,950 - 6.19T \log T - 0.78 (10^{-5}T^2) + 3.935 (10^6T^{-1}) + 102.37T$	

Entropy at 298°K, cal./deg./mole (corundum): 12.186

See Table b

Melting Point: 2313°K (2040°C)

Heat of Fusion, Kcal./mole: 26.0

Boiling Point: 2523°K (2250°C)

corundum (α-alumina) 3773°K (3500°C)

Heat of Vaporization: ———

Aluminum Oxide, Al<sub>2</sub>O<sub>3</sub> (page 3)

Transition Point: \_\_\_\_\_  
 Heat of Transition: \_\_\_\_\_  
 Heat of Sublimation: \_\_\_\_\_  
 Heat Content or Enthalpy: \_\_\_\_\_

b. HEAT CONTENT AND ENTROPY OF Al<sub>2</sub>O<sub>3</sub>(c)  
 (Base, corundum at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	2150	6.17	1300 . . . . .	27,730	38.87
500 . . . . .	4580	11.59	1400 . . . . .	30,800	41.14
600 . . . . .	7200	16.36	1500 . . . . .	33,890	43.27
700 . . . . .	9960	20.61	1600 . . . . .	36,990	45.27
800 . . . . .	12,810	24.42	1700 . . . . .	40,100	47.16
900 . . . . .	15,720	27.84	1800 . . . . .	43,220	48.94
1000 . . . . .	18,670	30.95	1900 . . . . .	46,350	50.63
1100 . . . . .	21,660	33.80	2000 . . . . .	49,490	52.24
1200 . . . . .	24,680	36.43			

Al<sub>2</sub>O<sub>3</sub>(c):

Enthalpy:  $H_T - H_{298.15} = 27.49T + 1.41 \times 10^{-5}T^2 + 8.38 \times 10^5T^{-1} - 11,132$   
 (0.5 percent; 298° - 1800°K)

Heat Capacity:  $C_p = 27.49 + 2.82 \times 10^{-5}T - 8.38 \times 10^5T^{-2}$

Heat Capacity, cal./deg./mole: (solid) 18.88

4, 9

See Table b for equation

Decomposition Temperature: 3800°K ± 200

8

Decomposition Products: 2AlO (gas) + O

63

For DTA see Addnl. Ref. 4

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	2148	2385	2549	2665	2874	2977	2040

X-Ray Crystallographic Data (α-corundum):

System      Space Group      a      c      Molecules/Unit Cell  
 hexagonal      D<sub>6h</sub><sup>2</sup>      5.56Å      22.55Å      2

1

Hygroscopicity: Powdered Al<sub>2</sub>O<sub>3</sub> readily absorbs moisture from the air.

29

Solubility Data:

In water at 29°C: 0.000098 g./100 g.  
 In hot water: insoluble  
 In acids and alkalies: very slightly soluble

1

**Aluminum Oxide,  $\text{Al}_2\text{O}_3$  (page 4)**

**Health Hazard:** High concentrations of dust may be irritating to the respiratory tract and cause Shaver's disease.

29

**M.A.C.:** 50 million particles/ft.<sup>3</sup>

12

**Safety Classifications:** \_\_\_\_\_

**Fire and Explosion Hazard:** \_\_\_\_\_

**Electrostatic Sensitivity:** \_\_\_\_\_

**Use in Pyrotechnics:** A small amount of alumina added to powdered red phosphorus maintains it in a free flowing condition and free from lumps.

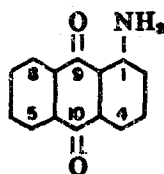
Spec. MIL-10825

Aluminum oxide is formed when aluminum or any of its compounds are burned in air, or in a sufficient amount of oxidizer or oxygen.

**Additional References:**

- 1) A. D. Mah, J. Phys. Chem. 61, 572 (1957) (gives the value for Heat of Formation as  $-400.48 \pm .25$  Kcal./mole)
- 2) "The Gaseous Species of the  $\text{Al-Al}_2\text{O}_3$  System," L. Brewer and A. Searcy, J. Am. Chem. Soc. 73, 5308 (1951). (disassociation pressures)
- 3) Ref. 64
- 4) "Differential Thermal Analysis of Organic Compounds," A. T. Perkins and H. L. Mitchell, Trans. Kansas Acad. Sci. 60, 437 (1957)
- 5) "The Density of Liquid Aluminum Oxide," A. D. Kirshenbaum and J. A. Cahill, J. Inorg. Nucl. Chem. 14, 283 (1960)

**1-AMINOANTHRAQUINONE, C<sub>14</sub>H<sub>9</sub>NO<sub>2</sub>**  
**(1-Amino-9,10-Dihydro-9,10-Dioxoanthracene;**  
**Fast Red Al;  $\alpha$ -Anthraquinonylamine, C.I. 37275, Azoic Component 36)**



Structural Formula:		
Specification No.:	MIL-D-3698	
Molecular Weight:	223.23	
Crystalline Form:	needles	
Color:	red	88V14
Density:	—	
Coefficient of Thermal Expansion:	—	
Heat of Formation:	—	
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	525°K (252°C) 528°K (253°C)	1 84
Heat of Fusion:	—	
Boiling Point:	sublimes	1, 88V14
Heat of Vaporization, Kcal./mole at 298°K and 1 atm.:	28.7 $\pm$ 0.1	Addnl. Ref. 1
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature:	—	
For DTA and TGA see Ref. 81	—	
Decomposition Products:	—	
Vapor Pressure:	—	
X-Ray Crystallographic Data:		
For absorption spectra see Ref. 68		
Hygroscopicity:	—	
Solubility Data:		Addnl. Ref. 2
In water, g./100 g. at 25°C:	0.00004	1, 28, 88V14
at 80°C:	0.0009	and V17
In ether, chloroform, benzene:	soluble	
In glacial acetic acid, 1 l. at 11.5°C:	dissolves 3.3 g.	

Refs.

1, 84, 48A

**1-Aminoanthraquinone,  $C_{14}H_9NO_2$  (page 2)**

In 92-96% $H_2SO_4$ :	dissolves with yellow color
In oleum, 20% $SO_3$ :	dissolves with red color
In concentrated HCl:	dissolves
Health Hazard:	---
Safety Classifications:	
OSM:	not listed
ICC:	not listed
Fire and Explosion Hazard:	---
Electrostatic Sensitivity:	---
Use in Pyrotechnics:	To color smoke mixtures red. Used in orange smoke mixtures.
Additional References:	
1) "A Radioactive Ionization Gauge and its Application to the Measure- ment of Latent Heat of Vaporization," J. H. Beynon and G. R. Nichol- son, J. Sci. Instr. 33, 376 (1956)	
2) J. Soc. Dyers Colourists 70, 68-77 (1954)	

# AMMONIUM NITRATE, $\text{NH}_4\text{NO}_3$ ,

Refs.

Percent Oxygen: 60

Specification No.: JAN-A-175

The specification covers grade I and grade II, which differ slightly in purity. Grade I has three classes differing in granulation.

Molecular Weight: 80.05

Crystalline Form: Five forms as follows:

Designation	System	Range °C
I ( $\epsilon$ )	regular (cubic) (isometric)	125.2 to 169.6
II ( $\delta$ )	rhombohedral or tetragonal	84.2 to 125.2
III ( $\gamma$ )	orthorhombic	32.1 to 84.2
IV ( $\beta$ )	orthorhombic	-16 to 32.1
V ( $\alpha$ )	tetragonal	-18 to -16

Color: colorless

Density, g./ml.: (solid) 1.725 at 25°C  
 $\epsilon$  1.594 at  $130 \pm 5^\circ\text{C}$   
 $\delta$  1.666 at  $93 \pm 5^\circ\text{C}$   
 $\gamma$  1.661 at  $40 \pm 1^\circ\text{C}$   
 $\beta$  1.725 at  $+25^\circ\text{C}$   
 $\alpha$  1.710 at  $-25 \pm 5^\circ\text{C}$

1, 43

Coefficient of Thermal Expansion:

Coeff. $\times 10^6$	677	852	920	982	1069	1113
Temp. °C	-60	-20	0	20	60	100

44

Heat of Formation, Kcal./mole at 298°K: ( $\epsilon$ ) -87.27  
-87.93

9

1A

Free Energy of Formation, Kcal./mole at 298°K: ( $\epsilon$ ) -45.82

Addnl. Ref. 11

Entropy, cal./deg./mole at 25°C: 36.0

Addnl. Ref. 11

See Table a

Melting Point: 442.8°K (169.7°C)

9

Heat of Fusion, Kcal./mole:

1.3

9

1.53

Addnl. Ref. 9

Boiling Point:

decomposes at 433°K  
(210°C)

1

Heat of Sublimation.

a. HEAT CONTENT AND ENTROPY OF  $\text{NH}_4\text{NO}_3(\text{c}, \text{l})$   
(Base,  $\alpha$ -crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
305.3 ( $\alpha$ ) . . .	240	0.80	393.4 ( $\delta$ ) . . .	4830	13.66
305.3 ( $\beta$ ) . . .	620	2.04	400 . . . . .	4900	13.83
325 . . . . .	1180	3.82	425 . . . . .	6040	16.60
350 . . . . .	1830	5.92	442.8 ( $\gamma$ ) . . .	6860	18.48
357.4 ( $\beta$ ) . . .	2100	6.52	442.8 (l) . . .	8160	21.42
357.4 ( $\gamma$ ) . . .	2420	7.41	450 . . . . .	8440	22.05
375 . . . . .	3020	9.05	500 . . . . .	10,360	26.09
398.4 ( $\gamma$ ) . . .	3820	11.12	550 . . . . .	12,290	29.77

 $\text{NH}_4\text{NO}_3(\alpha)$  :Enthalpy:  $H_T - H_{298.15} = 33.30T - 10,018$  (0.1 percent; 298° - 305.3°K)Heat Capacity:  $C_p = 33.50$ ;  $\Delta H_{305.3}$  (transition) = 380 $\text{NH}_4\text{NO}_3(\beta)$  :Enthalpy:  $H_T - H_{298.15} = 28.40 - 8051$  (0.1 percent; 305.3° - 357.4°K)Heat Capacity:  $C_p = 28.40$ ;  $\Delta H_{357.4}$  (transition) = 320 $\text{NH}_4\text{NO}_3(\gamma)$  :Enthalpy:  $H_T - H_{298.15} = 34.10T - 9767$  (0.1 percent; 357.4° - 398.4°K)Heat Capacity:  $C_p = 34.10$ ;  $\Delta H_{398.4}$  (transition) = 1010 $\text{NH}_4\text{NO}_3(\delta)$  :Enthalpy:  $H_T - H_{298.15} = 45.60T - 13,337$  (0.1 percent; 398.4° - 442.8°K)Heat Capacity:  $C_p = 45.60$  $\text{NH}_4\text{NO}_3(\text{l})$  :Enthalpy:  $H_T - H_{298.15} = 38.50T - 8887$  (0.1 percent; 442.8° - 550°K)Heat Capacity:  $C_p = 38.50$ 

Decomposition Temperature, °C: 210

1, 13

Decomposition Products: These vary with the conditions of decomposition or explosion. Many different equations for the decomposition reactions are given in the literature. Practically all involve oxides of nitrogen.

43

For DTA see Refs. 33, 47, and Addnl. Ref. 10

## Dissociation Pressure:

Press. mm. Hg.	3.25	7.45	11.55	15.80	27.0	41.0	M.P.
Temp. °C	188	205	216	223	237	249	169.6

Addnl. Ref. 11

See also Addnl. Ref. 3

Ammonium Nitrate,  $\text{NH}_4\text{NO}_3$  (page 3)

**b. X-RAY CRYSTALLOGRAPHIC DATA**

Designation	System	Space Group	a	b	c	Molecules/ Unit Cell
$\alpha$ or I	cubic		4.40			1
$\beta$ or II	tetragonal		5.75		5.00	2
$\gamma$ or III	orthorhombic	$V_b^{16}$	7.06	7.66	5.80	4
$\beta$ or IV	orthorhombic	$V_b^{16}$	5.75	5.45	4.96	2
$\alpha$ or V	rhombic	$V_b^{16}$	4.928	5.434	5.732	2

Hygroscopicity: Gain in weight at R.T. for reagent grade, after 24 hrs. exposure and to equilibrium in a static desiccator.

R.H. %	31		43		52		65	
	24 hrs.	Equil.	24 hrs.	Equil.	24 hrs.	Equil.	24 hrs.	Equil.
Gain mg./g.	0.8	0.5	0.5	0.5	0.7	1.0	131.6	—

Absorbed at 25°C by 2.0000 (C.P. material), 40-48 mesh:

Hrs.	3	5 1/4	7 3/4	16 1/2
g. $\text{H}_2\text{O}$ absorbed	0.1234	0.2087	0.2913	0.6387

Solubility Data:

Solubility, g./100 g. solvent (%):

Water		Alcohol		Nitric Acid			Pyridine		Acetic Acid	
°C	%	°C	%	°C	%	% $\text{HNO}_3$	°C	%	°C	%
0	118			0	45.1	30.0	25	Approx.	16.6	0.0
20	192	20	2.5	15	73.0	21.7	20-25		27.0	0.39
40	297	40	5	30	106	20.8			80.9	5.8
60	421	60	7.5	75	201	31.6			101.0	20.7
80	380	78	10.5						120.0	125
100	871									

Solubility, g./100 solvent:

In ethyl alcohol at 20°C:

3.8

In methyl alcohol at 20°C:

17.1

In acetone and  $\text{NH}_3$ :

slightly soluble

Health Hazard: Average or large doses may cause nausea and vomiting. Moderately toxic on ingestion or inhalation.

Safety Classifications:

OSM: Class 12. "When stored in an area where explosives may be projected into the nitrates, the regulations for Class 9 are applicable. When stored in an area with fire hazards only and separated by inhabited building distances from areas containing ammunition, ammonium nitrate may be stored in accordance with the regulations governing the storage of Class 2 solid propellants."

ICC: Oxidizing material; yellow label.



# Ammonium Nitrate, $\text{NH}_4\text{NO}_3$ (page 4)

**Fire and Explosion Hazard:** Many disastrous explosions have been attributed to ammonium nitrate. Although it is relatively insensitive as a high explosive by itself, if allowed to burn unconfined, its tendency to explode increases with pressure and the presence of oxidizable materials. Contamination with chlorides, nitrocompounds, sulfur, charcoal, melanic nitrates, metal powders, petroleum derivatives and oxidizable carbonaceous materials sensitizes ammonium nitrate, accelerates its decomposition and increases the violence of the reaction. Zinc or lead contamination lowers the decomposition temperature to below  $100^\circ\text{C}$ . Galvanized metals and lead solder should, therefore, not be used in the vicinity of ammonium nitrate. Fires involving ammonium nitrate should be vented to the greatest possible extent because air acts as a diluent for the hazardous gases, minimizing the probability of explosion. Fires should be fought with large quantities of water but never with steam.

See also Addnl. Ref. 12

## Electrostatic Sensitivity:

Heat of Combustion, Kcal./mole:

$Q_c = 50.3$

Addnl. Ref. 2

$Q_p = 49.4$

Heat of Explosion, cal./g.:

346

13

gas volume, cc./g.:

980

## Heat and Stability Tests:

$75^\circ\text{C}$  International Heat Test, % loss in 48 hours:

0.0

13

$100^\circ\text{C}$  Heat Test:

% loss first 48 hrs.:

0.74

13

% loss second 48 hrs.:

0.13

explosion in 100 hrs.:

none

Vacuum Stability Tests, gas evolved in 40 hrs.

at  $100^\circ$ ,  $120^\circ$ , and  $150^\circ\text{C}$ :

0.3 cc.

13

Explosion Temperature Test, 5 sec. point,  $^\circ\text{C}$ :

ignites at 465

13

Rifle Bullet Impact Test (at density of 1.2 g./ml.): unaffected in 100 trials

13

Sensitivity to Initiation, g. tetryl needed to initiate:

0.25

13

Trauzl Test, % TNT:

56

13

Friction Sensitivity:

unaffected by steel shoe

13

Impact Sensitivity: Effect of temperature on ground, C.P. Ammonium Nitrate.

13

Temp. $^\circ\text{C}$	P.A. Impact Test with 2 kg. weight, in.	(10% point)
25	31	
75	28	
100	27	
150	27	
175	12	

Ammonium Nitrate,  $\text{NH}_4\text{NO}_3$  (page 5)

Specific Heat: at °C	-150	-100	-50	0	50	100
cal./g./°C	0.189	0.590	0.364	0.397	0.414	0.428

13

Compatibility with Metals: In the presence of moisture, ammonium nitrate reacts with copper, iron, steel, brass, lead, and cadmium. See Addnl. Ref. 1

Uses in Pyrotechnics: as an oxidizing agent

Additional References:

- 1) "Military Explosives," TM-9-T011A-1-34, Departments of the Army and the Air Force (1955)
- 2) "Investigation of Sensitivity of Fertilizer Grade Ammonium Nitrate to Explosion," P. Macy et al., PATR-1658, Picatinny Arsenal, Dover, N.J. (1947)
- 3) "The Dissociation Pressure and Free Energy of Formation of Ammonium Nitrate," A. D. Little, Inc., J. Am. Chem. Soc. 76, (1954)
- 4) "On the Thermogravimetry of Analytical Precipitates," C. Duval and N. Xuong, Anal. Chem. Acta 6, 246 (1952)
- 5) DTA and TGA, Ref. 83
- 6) Ref. 54V2, general reference
- 7) "Hygroscopic Properties of Sodium, Potassium and Ammonium Nitrates, Potassium Chlorate and Mercury Fulminate," G. B. Taylor and W. C. Cope, Met. and Chem. Eng. 15, 141 (1916)
- 8) L. Médard and M. Thomas, Mém. poudres, 35, 155, 160 and 172 (1958)
- 9) "The Cryoscopic Heat of Fusion of Ammonium Nitrate," A. G. Keenan, J. Phys. Chem. 60, 1356 (1952)
- 10) "Differential Thermal Analysis of the Thermal Decomposition of Ammonium Nitrate," A. G. Keenan, J. Am. Chem. Soc. 77, 1379 (1955)
- 11) "The Dissociation Pressure and Free Energy of Formation of Ammonium Nitrate," G. Feick, J. Am. Chem. Soc. 76, 5858 (1954)
- 12) "Investigations on the Explosibility of Ammonium Nitrate," J. J. Burns et al., Bur. of Mines, RI 4894 (1953)
- 13) "The Thermal Decomposition of Ammonium Nitrate. Steady State Reaction Temperatures and Reaction Rate," G. Feick and R.M. Hainer, J. Am. Chem. Soc. 76, 5860 (1954)

# AMMONIUM PERCHLORATE, NH<sub>4</sub>ClO<sub>4</sub>

Refs.

Percent Oxygen: 54.47  
 Specification No.: JAN A-192  
 The specification covers two grades which differ in purity and two classes which differ in granulation: grade 1 is used in tracers; grade 2 is used in HC Smoke Mixtures.

Molecular Weight: 117.50  
 Crystalline Form: rhombic  
 Color: colorless  
 Density, g./ml.: (solid) 1.95  
 Coefficient of Thermal Expansion (cubical):  $\beta = (1/v) dv/dt$

1  
 1  
 1  
 1  
 Addnl. Ref. 4

Temp. °F	-25	0	25	50	75	100	125	150	175
$\beta \times 10^{-4}/^{\circ}\text{F}$	1.690	1.613	1.538	1.463	1.389	1.316	1.244	1.172	1.101

Heat of Formation, Kcal./mole at 298°K: -39.42  
 Free Energy of Formation, cal./g. at 298°K: -665  
 Kcal./mole: -78.14

9  
 13

Entropy:  
 Melting Point: decomposes above 423°K (150°C)  
 Heat of Fusion: decomposes before fusion  
 Boiling Point: decomposes  
 Transition Point: rhombic to cubic 513°K (240°C)

26VS  
 9

Ref. 72 cites  $\alpha$  to  $\beta$  at 28°C and  $\beta$  to  $\gamma$  at 360°C.

See also Ref. 47

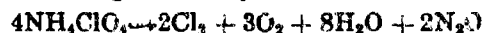
Heat of Sublimation: ———  
 Heat Content or Enthalpy: ———  
 Heat Capacity: ———

Decomposition Temperature and Products: Decomposes at a maintained temperature at 150°C. Decomposition products are NO<sub>2</sub> and ClO<sub>2</sub>.

14

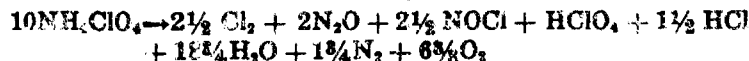
Decomposition begins at 130°C, becoming explosive at 380°C. The decomposition varies with the temperature. Below 300°C, decomposition is mainly according to the equation:

35.  
 Addnl. Refs.  
 5, 6, 7



Above 350° the proportion of nitric oxide increases and becomes appreciable. Above 350° the following equation represents decomposition:

cited by  
 Ref. 72



The activation energy for decomposition varies with temperature. The following are several values for activation energy: 29.6 Kcal./mole below 240°C and 18.9 Kcal./mole above 240°C. Between 400° and 440°C the value is 73.4 Kcal./mole.

47

For DTA see Ref. 47

**Ammonium Perchlorate,  $\text{NH}_4\text{ClO}_4$  (page 2)**

**Vapor Pressure:**

**X-Ray Crystallographic Data:**

System	Space Group	a	b	c	Molecules/Unit Cell
rhombic	$V_1^h$	9.202	5.816	7.447	4
		9.13	5.17	7.47	4
	$D_{2h}^h$	9.231	5.813	7.453	4

1  
Addnl. Ref. 8  
97V7

**Hygroscopicity:** Gain, in mg./g. of a purified sample at equilibrium at 70°F, after equilibrium had been established in a vacuum desiccator:

R.H.%	(	75	86	93
Gain mg./g.	0.5	0.5	0.4	0.8

32

**Critical R.H.:** 87.0% at 25°C

**Solubility:** In water, g./100 cc. of saturated solution:

13

Temp. °C	0	25	60	100
Sol.	12	20	39	83

**Solubility in Nonaqueous Solvents at 25°C:**

65, 77

Solvent	g./100 g. solvent
acetone	2.26
ethyl acetate	0.032
ethyl alcohol	1.908
ethyl ether	insol.
methyl alcohol	6.85

**Health Hazard:** Moderate. Irritating to skin and mucous membranes.

12, 65

Evolves highly toxic fumes when heated to decomposition.

Moderately toxic on ingestion or inhalation.

Weak muscular poison; may cause convulsions. Harmful to thyroid.

93, 72

**Safety Classifications:**

OSM: Class I; Class II when not packed in original containers or equivalent.

ICC: Oxidizing material; yellow label. Listed under "Explosives and Other Dangerous Articles."

**Fire and Explosion Hazard:** A powerful oxidizer, explodes violently when heated with sulphur, organic matter, or finely divided metals, particularly magnesium and aluminum. Exploded by shock. Fires involving ammonium perchlorate alone may be fought with water.

12, 14

**Electrostatic Sensitivity:**

**Specific Volume:**  $V_s = a + bt + ct^2$

Addnl. Ref. 4

where  $a = 0.5074 \text{ cm}^3/\text{g.}$

$b = 0.819 \times 10^{-4} \text{ cm}^3/\text{g.}/^\circ\text{F}$

$c = 0.704 \times 10^{-7} \text{ cm}^3/\text{g.}/(^\circ\text{F})^2$

**Ammonium Perchlorate,  $\text{NH}_4\text{ClO}_4$  (page 3)**

**Explosive Data:**

65, 72

**Sensitivity:** Requires the equivalent of 10 mg. of mercury fulminate or an XC-32. Very insensitive as an explosive but more sensitive than Na, K, and Mg perchlorates. Drop test—min.: 86 in. for an 11-lb. wt. Insensitive to severe friction. Heating small quantities does not result in an explosion. The temperature developed on explosion is 1308°C and the heat liberated, 344.5 cal./g.

**Brisance:** Trauzl lead block test, expansion in cc.: 140.2, equivalent to one-quarter that of 40% N.G. dynamite.

**Velocity of Detonation,** in 60 mm. diameter iron tube and detonated with five No. 8 caps: 3800 m./sec.

100°C Heat Test		Vacuum Stability Test		
loss first 48 hrs. %	0.02	cc. of gas evolved from 5 g. in 40 hrs. at		13
loss second 48 hrs. %	0.00	100°C	0.13	
explosion in 100 hrs.	none	120°C	0.20	
		150°C	0.32	

**200-Gram Bomb Sand Test,** g. sand crushed: 6.0 13

**Sensitivity to Initiation:** requires 0.25 grams of tetryl 13

**Explosion Temp. in 5 sec., °C:** 435 13

**Temperature of Explosion, °C:** (est.) 1084 72

**Impact Sensitivity, 2-kg. weight:** 13

Bureau of Mines app., cm. (10% point): 67

Picatinny Arsenal app., in. (10% point): 24

Sample weight, mg.: 24

**Sensitivity to Friction:** Bureau of Mines app., steel shoe; 100 trials—no explosion or ignition, one snap. 72

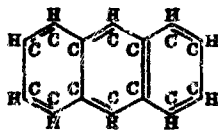
**Use in Pyrotechnics:** as an oxidizing agent

**Additional References:**

- 1) "The Use of Differential Thermal Analysis for Investigating the Effects of High Energy Radiation on Crystalline Ammonium Perchlorate," E. Freeman and D. Anderson, *J. Phys. Chem.* 63, 1344 (1959)
- 2) "Apparatus for Observing Physical Changes at Elevated Temperatures," V. Hogan and S. Gordon, *Anal. Chem.* 32, 573 (1960)
- 3) "The Thermal Decomposition of Ammonium Perchlorate," L. Bircumshaw and B. Newman, *Proc. Roy. Soc. A227*, 115 (1954); also *A227*, 228 (1955)
- 4) Report Q PR No. 492, Aerojet General Corporation, Sacramento, Calif.
- 5) L. L. Bircumshaw and T. R. Phillips, *J. Chem. Soc.* 1957, 4741 (1957)
- 6) "The Crystal Structure of Ammonium Perchlorate- $\text{NH}_4\text{ClO}_4$ ," K. Venkatesan, *Proc. Indian Acad. Sci.* 46A, 134 (1957)

**ANTHRACENE,  $C_{14}H_{10}$  ( $(CH_2)_2C_6H_4$ )**  
(Green oil, *P*-Naphthalene)

Structural Formula:



Specification No.

JAN-A-202

The specification covers a technical grade in two classes, a and b, which differ in granulation.

Molecular Weight:

178.22

Crystalline Form:

monoclinic

Color:

colorless with violet  
fluorescence

Density, g./ml.:

(solid) 1.25

Coefficient of Thermal Expansion, cubical,  
over the range 20–180°C:

$$V_{t_2} = V_1 [1 + \alpha (t_2 - t_1) + \beta (t_2 - t_1)^2]$$

where  $\alpha = 213 \times 10^{-6}$  and  $\beta = 3.10 \times 10^{-7}$

Heat of Formation, Kcal./mole at 25°C at constant  
pressure:

25.53

Free Energy of Formation:

—

Entropy, cal./deg./mole at 298.1°K:

49.6

Melting Point:

490°K (217°C)

Heat of Fusion, cal. (15°/g.) at 216.55°C:

38.7

Boiling Point:

627°K (354–5°C)  
339.9°C

Heat of Vaporization, Kcal./mole:

13.10

Transition Point:

—

Heat of Sublimation:

—

Heat Content or Enthalpy:

—

Heat Capacity:

—

Specific Heat:

Temp. °K	94.4	124.8	193.2	254.4	297.2	20–100	20–210	liquid
cal./g.	0.95	0.117	0.177	0.239	0.278	0.312	0.3688	0.509

Decomposition Temperature:

—

Decomposition Products:

—

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	145.0	187.2	217.5	250.0	310.2	342	217.5

Refs.

1, 12

1

29

1

Addnl. Ref. 4

Addnl. Refs.  
1, 2

1

1

1

31A

57V13

57V13

1

**Anthracene,  $C_{14}H_{10}$  (page 2)**

**X-Ray Crystallographic Data:**

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell</i>	
monoclinic	$C_2^h$	8.58	6.02	11.18	$\beta = 125^\circ$	2	57, 85
		8.561	6.026	11.163	$\beta = 124^\circ 42'$	2	
Hygroscopicity:					very slight		
Solubility Data, g./100 ml. In water:					insoluble		1
In alcohol at 160°C:					0.076		
at 78°C:					0.88		
In ether:					1.189		
In $CHCl_3$ :					1.767		
In $CS_2$ :					1.500		
In benzene at 80°C:					7.5		
Health Hazard: Purified white material is considered non-toxic. However, the impure technical product may be carcinogenic because of impurities present. Avoid repeated contact or inhalation of dusts or vapors. As a chronic local irritant it is considered severely toxic.							12, 25, 93
Fire and Explosion Hazard: Burns when heated in air. Vapors may explode when ignited in air. Gives off acrid fumes. Reacts with oxidizing materials. To fight fire, use water, foam, $CO_2$ , dry chemicals, or $CCl_4$ .							12, 26, 29, 67
Safety Classifications:							
OSM:					not listed		
ICC:					not listed		
Electrostatic Sensitivity: Anthracene dust clouds can be ignited and exploded by an electric spark.							Addnl. Ref. 3
Anthracene darkens on exposure to light.							29
Heat of Combustion, Kcal./mole at 20°C:					1700.4		1
Boiling Point, °F (closed cup):					250		75
(open cup):					385		
Autoignition Temperature, °F:					881		26, 75
Ref. 71 gives 472°C in air							
Explosive Limits in Air, % by vol., lower:					0.62		67
Use in Pyrotechnics:					as a fuel		

**Additional References:**

- 1) J. Am. Chem. Soc. 68, 2727 (1946)
- 2) J. Am. Chem. Soc. 74, 1571 (1952)
- 3) A. Van Dussen, Rec. trav. chim. 54, 873 (1935)
- 4) W. Klem et al., Zeit. anorg. Chem. 176, 10 (1928)

# ANTIMONY SULFIDE (tri), Sb<sub>2</sub>S<sub>3</sub>

(Antimony Trisulfide, Antimony Black, Black Antimony, Stibnite, Antimonite, Needle Antimony, Sulfur Gold, Sulfuret of Antimony, Antimony Glance)

Specification No.:	MIL-A-159											
Molecular Weight:	339.72											
Crystalline Form:	rhombic											
Color:	black or red											
For color changes see Ref. 54V9												
Density, g./ml.:	(solid) 4.64	1										
Coefficient of Thermal Expansion:	—											
Heat of Formation, Kcal./mole at 25°C:	(c) black, -43.5 (amor.) orange, -33.0	1 1										
Free Energy of Formation, Kcal./mole at 300°K (27°C):	-36.0	40V2										
Entropy, cal./deg./mole at 298.16°K:	(c) 39.6 (c) 30.3 ± 4.0	3 24										
Melting Point:	823°K (550°C)	1										
Sinters in air at 440°C, melts at 510°C												
Heat of Fusion, 15° cal./g. at 540°C:	17.6	1										
Boiling Point: Volatizes above its melting temperature and can be distilled without decomposition		20V3 54V9										
Heat of Vaporization:	—											
Transition Point: See Ref. 54V9												
Heat of Transition, Kcal./mole:	violet to black, 4.3 orange-red to black, 5.6	54V9										
Heat of Sublimation, Kcal./mole at M.P.:	51.2	24, 40V2										
Sublimation Temperature, °C:	380	54V9										
Heat Content or Enthalpy:	—											
Heat Capacity, cal./deg./mole at 298-821°K:	C. = 24.2 + 13.2T	24										
Decomposition Temperature: When heated in air, above 176°C, it is slowly converted to the oxide.	—	15										
Decomposition Products:	loses S; takes up O											
Vapor Pressure:												
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%;">Press. mm.</td> <td style="width: 25%;">about 0.033</td> <td style="width: 25%;">1.17</td> <td style="width: 25%;">13.45</td> <td style="width: 25%;">244</td> </tr> <tr> <td>Temp. °C</td> <td>400</td> <td>500</td> <td>650</td> <td>850</td> </tr> </table>		Press. mm.	about 0.033	1.17	13.45	244	Temp. °C	400	500	650	850	44V18B
Press. mm.	about 0.033	1.17	13.45	244								
Temp. °C	400	500	650	850								

**X-Ray Crystallographic Data:**

System	Space Group	a	b	c	Molecules/Unit Cell	
rhombic	V <sub>h</sub> <sup>h</sup>	11.39	11.48	3.88	4	1
orthorhombic	V <sub>h</sub> <sup>h</sup>	11.23	11.31	3.84	4	97V5

Hygroscopicity: not hygroscopic 20

*Refs.*



**Antimony Sulfide (tri),  $\text{Sb}_2\text{S}_3$  (page 2)**

**Solubility Data:**

In water at 18°C:	$0.175 \times 10^{-6}$ g./ml.	1
In hot water:	decomposes	
In alk., $\text{NH}_4\text{HS}$ , $\text{K}_2\text{S}$ , $\text{HCl}$ :	soluble	
In acetic acid:	insoluble	

**Health Hazard:** Irritates the skin and mucous membranes. May cause gastrointestinal upsets. A poison with symptoms similar to arsenic. A cardiac and nervous depressant. Antimony poisoning is detectable in the blood and by liver functioning. 12, 21

**M.A.C.:** 0.5 14, 17, 17

**Safety Classification:**

**OSM:** Inert and presents no particular fire or toxic hazard as used in Ordnance establishments.

See also Addnl. Refs. 1 and 2

**Fire and Explosion Hazard:** Dangerous; when heated to decomposition or on contact with acid or acid fumes, it emits highly toxic fumes of oxides of S and Sb. It reacts with steam or water and produces toxic and inflammable vapors. Reacts vigorously with oxidizing materials such as chlorates or perchlorates. 12

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:** Antimony sulfide is used as a fuel. It imparts a pale green color to burning compositions. 20

**Additional References:**

- 1) C.A. 42, 1711 (1948)
- 2) C.A. 45, 9748 (1951)

## ASPHALTUM

(Gilsonite, Asphalt, Asphaltite, Earth Pitch,  
Uintate or Uintahite, Mineral Rubber)

Specification No.:	JAN-A-356	Refs.
Molecular Weight:	variable mined material, about 250	17V2 Addnl Ref. 1
Crystalline Form:	amorphous	Addnl. Ref. 1
Color:	brown to black, leaves brown streak	
Density, g./ml.:	(solid) 1.05-1.10	Addnl. Ref. 1
Coefficient of Thermal Expansion, cubical:	$5-7 \times 10^{-4}$	1
Heat of Formation:	—	
Free Energy of Formation:	—	
Entropy:	—	
Softening Point, specification min.:	398°K (125°C)	
Heat of Fusion:	—	
Boiling Point:	< 743°K (470°C)	12
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature and Products:	May be distilled to about 550°F. Above this temperature an exothermic reaction takes place with the rapid evolution of gaseous products. Between 475° and 650°F an oily distillate is obtained.	Addnl. Ref. 1
Vapor Pressure:	—	
X-Ray Crystallographic Data:	—	
Hygroscopicity:	nonhygroscopic	
Solubility Data:	Insoluble in water, alcohol, acids, and alkalis. Soluble in petroleum, ether, and acetone. The specification requires the following: CCl <sub>4</sub> —10% min., petroleum ether—30% min., and CS <sub>2</sub> —99% min.	29
Health Hazard:	Fumes or dust may irritate the eyes and respiratory tract. Moderately toxic; acute or chronic irritant.	29, 93
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard:	slight	75
Flash Point (closed cup) °F:	400	
(open cup) °F:	505	
Autoignition Temperature:	905	
To fight fire use foam, CO <sub>2</sub> , dry chemical, or CCl <sub>4</sub> .		

## Asphaltum (page 2)

### Electrostatic Sensitivity:

Asphaltum is formed from petroleum as the result of heat and pressure working over geologic time. The type of asphalt called for in the specification is known as gilsonite or uintate and is found mainly in Utah and Colorado. Chemically, gilsonite consists mainly of saturated hydrocarbons substantially free from oxygenated bodies with little or no crystallizable paraffins. Gilsonite is marketed in two grades known as "selects" or "firsts" and "seconds." The "firsts" are from the center of the vein and have a lustrous conchoidal fracture. The "seconds" are from near the walls of the vein and show a semiconchoidal and semilustrous fracture. They are differentiated on the basis of softening point and behavior in petroleum solvents. Although gilsonite is a mined product it shows fairly uniform characteristics as follows:

Fracture:	conchoidal	
Luster:	bright to fairly bright	
Hardness on Moh's scale:	2	
Fusing point, Kramer and Sarnow Method, °F:	230-350	
Ball and Ring Method, °F:	270-400	
Volatile in 5 hrs. at 325°F, %:	not less than 2	
400°F, %:	not less than 4	
500°F, %:	not less than 5	
Fixed Carbon, %:	10-20	
Solubility in CS <sub>2</sub> , %:	greater than 98	
Non-mineral matter, insoluble %:	0-1	
Mineral matter, %:	trace to 1	
Carbenes, %:	0-0.5	
Soluble in 88° petroleum naphtha, %:	10-60	
Hydrogen, %:	8.5-10	
Sulfur, %:	0.3-0.5	
Solid paraffines, %:	0-trace	
Sulfonation residue, %:	85-95	
Saponifiable matter, %:	trace	
Minimum Energy Required for Ignition of Dust		26V1
Cloud by Electric Sparks, millijoules:	25	
Ignition Temperature of Dust Cloud, °C:	560	26V1
Minimum Explosive Concentration of Dust:	20 mg./l. 20	26V1
Use in Pyrotechnics: Asphaltum is used as a fuel and binder. It may act as a desensitizer and waterproofing agent.		

### Additional References:

- 1) "Asphalts and Allied Substances," H. Abraham, D. Van Nostrand Co., Inc., New York (1960)
- 2) "The Science of Petroleum." Vol. 4, A. E. Dunstan et al., eds., Oxford University Press, New York (1938)

## AURAMINE HYDROCHLORIDE

(4,4'-Dimethylinobenzeneimine Hydrochloride,  
4,4'-bis (Dimethylamine) Benzhydrylideneimine Hydrochloride,  
Imido-tetramethyldiamidodiphenylmethane Hydrochloride,  
Auramine O, C.I. 41000, C.I. Basic Yellow 2)

Structural Formula:  $[(CH_3)_2NC_6H_4]_2C:NH_2Cl$  or  $C_{17}H_{22}N_2Cl$  or  
 $(H_3C)_2N \langle \text{benzene ring} \rangle C = \langle \text{benzene ring} \rangle N(CH_3)_2$  or  $(H_3C)_2N \langle \text{benzene ring} \rangle C = \langle \text{benzene ring} \rangle = N(CH_3)_2$   
 $NH \cdot HCl$   $NH_2$   $Cl$

Specification No.: MIL-A-3664 (1957)

Molecular Weight: 303.84

Crystalline Form: flakes

Color: yellow

Apparent Density, g./ml.:  $0.35 \pm 0.1$

Coefficient of Thermal Expansion: —

Heat of Formation: —

Free Energy of Formation: —

Entropy: —

Melting Point:  $540^\circ K$  ( $267^\circ C$ )

$538^\circ K$  ( $265^\circ C$ )

Heat of Fusion: —

Boiling Point: —

Transition Point: —

Heat of Sublimation: —

Heat Content or Enthalpy: —

Heat Capacity: —

Decomposition Temperature: —

Decomposition Products: The aqueous solution decomposes at about  $70^\circ C$  to  $NH_4Cl$  and tetramethyldisiminobenzophenone (Michler's Ketone).

The same reaction takes place in cold dilute acid.

Increase in temperature and acidity increases the rate of hydrolysis.

Vapor Pressure: —

X-Ray Crystallographic Data: —

Hygroscopicity: —

Solubility:

In water and alcohol: slightly soluble

In chloroform: readily soluble

In ether or pyridine: almost insoluble

Hydrolyzed by hot water (see Decomposition Products.)

*Refs.*

83 (No. 425),  
82, 48A

88V14

Spec.

88V14

Addnl. Ref. 1

52

Addnl. Ref. 2

88V14 II

**Auramine Hydrochloride (page 2)**

**Health Hazard:** Carcinogenic on chronic exposure, moderately toxic. The spec. requires that each container be labeled, "CAUTION: AVOID SKIN CONTACT. USE WITH ADEQUATE VENTILATION." 92, 93

**Safety Classifications:**

OSM:	not listed
ICC:	not listed

**Fire and Explosion Hazard:** \_\_\_\_\_

**Electrostatic Sensitivity:** \_\_\_\_\_

**Use in Pyrotechnics:** To produce yellow colored smoke.

**Additional References:**

- 1) J. Chem. Soc. 461 (1940) (also gives absorption spectra)
- 2) J. Am. Chem. Soc. 46, 2848 (1924) ; C.A. 18, 3872 (1924)

**BARIUM CARBONATE, BaCO<sub>3</sub>**  
(Witherite)

Specification No.:	JAN-B-624	Refs.
Molecular Weight:	197.37	
Crystalline Form:	(witherite, $\gamma$ ) rhombic ( $\alpha$ ) hexagonal	1
Color:	white	1
Density, g./ml.:	(solid) 4.48 (witherite) 4.29	1A 31A
Coefficient of Thermal Expansion, cubical:	$2.33 \times 10^{-5}$ (value used commercially)	37
Heat of Formation, Kcal./mole at 298°K:	(c) -291.3	1, 9
Free Energy of Formation, Kcal./mole, at 298°K:	(c) -272.2	1, 9
Entropy, cal./deg./mole, at 298°K:	(c) 26.8	3, 7, 9
See table below		
Melting Point, at 90 atm.:	2013°K (1740°C) fuses at 1361°C with loss of CO <sub>2</sub>	1 52V1
Heat of Fusion:	—	
Boiling Point:	decomposes at 1723°K (1450°C) with loss of CO <sub>2</sub>	22
Heat of Vaporization:	—	
Transition Point:	$\alpha$ 1079°K (806°C) $\rightarrow$ $\beta$ $\beta$ 1241°K (968°C) $\rightarrow$ $\gamma$ $\alpha$ 4490 $\rightarrow$ $\beta$ 730 $\rightarrow$ $\gamma$	4 4
Heat of Transition, cal./mole:		
Heat of Sublimation:		4

**HEAT CONTENT AND ENTROPY OF BaCO<sub>3</sub>(c)**  
(Base,  $\alpha$ -crystals at 298.15°K)

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	230.0	6.61	1100 . . . . .	27,060	39.17
500 . . . . .	4730	12.03	1200 . . . . .	30,760	42.39
600 . . . . .	7330	16.76	1241 ( $\beta$ ) . . .	32,270	43.62
700 . . . . .	10,080	21.00	1241 ( $\gamma$ ) . . .	33,000	44.21
800 . . . . .	12,980	24.37	1300 . . . . .	35,240	45.38
900 . . . . .	16,020	28.45	1400 . . . . .	39,040	48.79
1000 . . . . .	19,190	31.79	1500 . . . . .	42,840	51.41
1079 ( $\alpha$ ) . . .	21,790	34.29	1600 . . . . .	46,640	53.86
1079 ( $\beta$ ) . . .	26,280	38.45			

Barium Carbonate, BaCO<sub>3</sub> (page 2)

BaCO<sub>3</sub>(α) :

Enthalpy:  $H_T - H_{298.15} = -21.50T + 5.53 \times 10^{-5}T^2 + 3.91 \times 10^6T^{-1} - 8213$   
(0.5 percent; 298° - 1079°K)

Heat Capacity:  $C_p = 21.50 + 11.06 \times 10^{-5}T - 5.91 \times 10^{-8}T^2$

BaCO<sub>3</sub>(β) :

Enthalpy:  $H_T - H_{298.15} = 37.00T - 15,644$  (0.1 percent; 1079° - 1241°K)

Heat Capacity:  $C_p = 37.00$

BaCO<sub>3</sub>(γ) :

Enthalpy:  $H_T - H_{298.15} = 38.00T - 14,160$  (0.1 percent; 1241 - 1600°K)

Heat Capacity:  $C_p = 38.00$

Decomposition Products:

For pyrolysis see Ref. 45 and Addnl. Ref. 1

Decomposition Products:

BaO + CO<sub>2</sub>

Dissociation Pressure:

Press. mm.	0	5	45	120	240	340	450	675	760
Temp. °C	397	1017	1067	1097	1137	1157	1177	1197	1200

54V3

For Dissociation Pressure see also Addnl. Ref. 3

Calculated Dissociation Pressures to BaO + CO<sub>2</sub> above 1079°K are given by

$$\log P_{\text{mm.}} = \frac{13,075}{T} + 7.668$$

Addnl. Ref. 3

Vapor Pressure of CO<sub>2</sub> at 1100°C:

20 mm.

52V1

At 1600°C the loss of CO<sub>2</sub> is complete

See also Addnl. Ref. 2

X-Ray Crystallographic Data:

System	Space Group	a	b	c	Molecules/Unit Cell
rhombic	V <sub>h</sub> <sup>h</sup>	5.29	8.88	6.41	4

1

Hygroscopicity:

Solubility Data: In 100 ml. water:

α = 0.002 g. at 20°C  
0.006 g. at 100°C  
β = 0.0022 g. at 18°C  
0.0065 g. at 100°C

1

In acids, NH<sub>4</sub>Cl:

soluble

In alcohol:

insoluble

Health Hazard: Poisonous. Irritates mucous membranes. It produces dermatitis and causes hemorrhages in the gastrointestinal tract and kidneys.

12, 29

M.A.C., mg./m.<sup>3</sup>:

0.5

**Barium Carbonate, BaCO<sub>3</sub> (page 3)**

**Safety Classifications:**

OSM:	not listed
ICC:	not listed
Fire and Explosion Hazard:	none listed

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:** BaCO<sub>3</sub> is used as a retardant. It imparts some green color to a burning composition. 17

**Additional References:**

- 1) "Differential Thermal Analysis Studies of Ceramic Materials: Characteristic Heat Effects of Some Carbonates," M. Gruver; J. Am. Ceram. Soc. 33, 96 (1950)
- 2) G. Tammann and W. Pape, Zeit. anorg. Chem. 127, 50 (1923)
- 3) "Experimental Heat Contents of SrO, BaO, CaO, BaCO<sub>3</sub>, and SrCO<sub>3</sub> at High Temperatures. Dissociation Pressures of BaCO<sub>3</sub> and SrCO<sub>3</sub>," J. J. Lander, J. Am. Chem. Soc. 73, 5794 (1951)



# BARIUM CHLORATE, Ba(ClO<sub>3</sub>)<sub>2</sub>

Refs.

Percent Oxygen:	31.55						
Specification No.:	not listed						
Molecular Weight:	304.27						
Crystalline Form:	—						
Color:	colorless						
Density, g./ml.:	(solid) 3.856 at 24°C	12					
Coefficient of Thermal Expansion:	—						
Heat of Formation, Kcal./mole at 298°K:	(c) -181.7	1A, 9					
Free Energy of Formation, Kcal./mole at 298°K:	(c) -133.1	44S30					
Entropy, cal./deg./mole at 298°K:	53.7	44S30					
Melting Point:	414	1A					
Heat of Fusion:	—						
Boiling Point:	—						
Transition Point:	—						
Heat of Sublimation:	—						
Heat Content or Enthalpy:	—						
Heat Capacity of Ba (ClO <sub>3</sub> ) <sub>2</sub> · H <sub>2</sub> O, cal./deg./mole:							
C <sub>p</sub> = 50.6 (289–320°K)		4					
Decomposition Temperature: Decomposition starts at about 300°C.		54V2					
For DTA see Ref. 33							
Decomposition Products:	Ba (ClO <sub>4</sub> ) <sub>2</sub> + 2O <sub>2</sub>	54V2					
Vapor Pressure:	—						
X-Ray Crystallographic Data for Ba (ClO <sub>3</sub> ) <sub>2</sub> · H <sub>2</sub> O:							
System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell	
monoclinic	C <sub>2h</sub>	8.86	7.80	9.35	β = 94° ± ½°	4	Addnl.
See also Addnl. Ref. 1							
Hygroscopicity:	—						
Solubility Data:							
In water (g./100 g. solvent):					20.35 at 0°C		31
					84.8 at 80°C		
Health Hazard: Poisonous when taken by mouth. Very toxic in contact with the skin, when inhaled as a dust, or when ingested.							29, 14
M.A.C., mg./m. <sup>3</sup>					0.5		12
Safety Classifications							
OSM: Class 1, in original container or equivalent. Class 2, not in original container or equivalent.							
ICC: Oxidizing material, yellow label. Listed under Explosives and Other Dangerous Articles.							
M.C.A.: Warning label required.							

**Barium Chlorate,  $\text{Ba}(\text{ClO}_3)_2$  (page 2)**

**Fire and Explosion Hazard:** Considered more dangerous to store than  $\text{KClO}_3$ . 14, 12

Should be stored away from flammable materials because of possible fire and explosion.

**Electrostatic Sensitivity:**

**Ignition Temperature, °C:** (5 second point) 506 33

**Activation Energy, Kcal./mole:** 45.7 33

**Use in Pyrotechnics:**

To impart a green color to burning compositions, and as an oxidizing agent.

**Additional References:**

- 1) "Determination of the Structure of Metallic Chlorates by Infrared Spectroscopy," T. Dupuis, *Compt. rend.* 242, 2922 (1956). C. A. 50, 15,236 (1956)
- 2) "Unit Cell and Space Group of Barium Chlorate Monohydrate," G. Kartha, *Current Science (India)* 20, 151 (1951). C. A. 46, 4312 (1952)

# BARIUM CHLORIDE, BaCl<sub>2</sub>

Specification No.:	not listed
Molecular Weight:	208.27
Crystalline Form:	monoclinic
Color:	colorless
Density, g./ml.:	(solid) 3.856 at 24°C

Refs.

1A

1A

1A

## Density of Molten BaCl<sub>2</sub>

Temp. °C	964	975	1025	1050	1085	1100
Density	3.057	3.052	3.015	3.108	3.087	3.076

44S30

For the temp. range 964°-1100°C the density is given by the formula  
 $D = 3.032 - 0.00070(t - 1000)$

Note: See refs. for additional density formulas

Coefficient of Thermal Expansion, cubic,  
 20-170°C:

$60 \times 10^{-6}$

44S30

Heat of Formation, Kcal./mole at 298°K:

(c) -205.56

1A, 6

Free Energy of Formation, Kcal./mole at 298°K:

(c) -193.8

1A, 9

Entropy, cal./deg./mole at 298°K:

30

1A, 9

Melting Point, °K:

1235

9

Heat of Fusion, Kcal./mole at 1235°K:

5.4

9, 24A

Boiling Point, °C:

1560

1A, 31A

Heat of Vaporization, Kcal./mole:

50.0

24A

57

41

Transition Point, monoclinic ( $\alpha$ ) to cubic  $\beta$ :

1198°K

1A, 9, 6

920-930°C

44S30

Heat of Sublimation, Kcal./mole:

57

44S30

Heat Content or Enthalpy:

---

Heat Capacity, cal./deg./mole:

(solid) 18.0 at 25°C

$C_p = 17.00 + 334 \times 10^{-5}T$  (estd., 298-1198°K)

4

Decomposition Temperature: None up to 1000°C  
 (max. experimental temp.)

33

Decomposition Products:

---

Vapor Pressure (liquid BaCl<sub>2</sub>):

Press. mm.	about 0.7	4.4	6.2	8.5	760
Temp. °K	1342.9	1435.2	1465.9	1486.7	1835

44S30

## X-Ray Crystallographic Data:

	System	Space Group	a	b	c	Molecules/ Unit Cell
BaCl <sub>2</sub>	orthorhombic	V <sub>2h</sub> <sup>16</sup>	9.323	7.823	4.705	4
BaCl <sub>2</sub> ·H <sub>2</sub> O	rhombic	D <sub>2h</sub> <sup>16</sup>	4.51	9.02	11.28	

13, 36, Addnl.  
 Ref. 1

**Barium Chloride, BaCl<sub>2</sub> (page 2)**

<b>Hygroscopicity:</b>	slight	44S30
<b>Solubility Data:</b>		
In H <sub>2</sub> O, g./100 ml.:	31 at 0°C 59 at 100°C	31A
In HCl, HNO <sub>3</sub> :	slightly soluble	
In alcohol:	insoluble	
<b>Health Hazard:</b>		
Extremely toxic. Fatal dose 0.8 to 0.9 g.		29
<b>Safety Classifications:</b>		
OSM:	not listed	
ICC:	not listed	
<b>Fire and Explosion Hazard:</b>	none listed	
<b>Electrostatic Sensitivity:</b>	—	
<b>Use in Pyrotechnics:</b> BaCl <sub>2</sub> results from the burning of some barium compounds in the presence of chlorine compounds.		
<b>Additional References:</b>		
1) C.A. 44, 397 (1950)		

**BARIUM CHROMATE, BaCrO<sub>4</sub>**  
(Lemon Chrome, Ultramarine Yellow, Baryta Yellow, Gelbin)

*Refs.*  
1, 11, 25

Percent Oxygen: 25.28  
Specification No.: MIL-B-550  
The specification covers two grades; grade A is for use in delay and non-gaseous powder, grade B for use in pyrotechnic mixtures.

Molecular Weight: 253.37  
Crystalline Form: rhombic  
Color: yellow  
Density, g./ml.: 4.498  
Coefficient of Thermal Expansion (calculated from lattice constants), linear:

1  
1  
1  
44S30 sup

Temp. Range °C	10-70	70-130	130-190	190-250	10-250
Coeff. $\times 10^6$	1.75	1.73	1.57	1.65	1.67

Heat of Formation, Kcal./mole at 298°K: (c) -341.3  
Free Energy of Formation, Kcal./mole at 298°K: -315.95  
Entropy, cal./deg./mole at 298°K: 34.7  
Melting Point: decomposes (see below)  
Heat of Fusion: decomposes (see below)  
Boiling Point: decomposes (see below)  
Transition Point: —  
Heat of Sublimation: —  
Heat Content or Enthalpy: —  
Heat Capacity: —

1, 9  
78  
78

Decomposition Temperature and Products: When heated, starts to lose weight at about 60°C. On further heating very slowly loses weight even up to 1015°C, at which point it is a mixture of the yellow chromate and green chromite. Even at this temperature the loss is less than 1%.

Addnl. Ref. 1

Vapor Pressure: —

X-Ray Crystallographic Data: —

Hygroscopicity: Gain in weight (%) at 70°F of specification grade A material

Exposure hrs.	Relative Humidity, %		
	52	75.8	90
24	0.06	0.05	0.25
48	0.06	0.06	0.27
72	0.06	0.05	0.27
144	0.06	0.09	0.28
168	0.06	0.09	0.28

33

Solubility Data: In water, g./100 g.: 0.00034<sup>16\*</sup> and 0.00044<sup>23\*</sup>  
In mineral acids: soluble

1

**Barium Chromate, BaCrO<sub>4</sub> (page 2)**

**Health Hazard:** Poisonous. Has a corrosive action on the skin and mucous membranes. Produces dermatitis. 12, 29

The specification requires that all containers be marked with the following precautionary marking: "AVOID INHALATION OF DUST. AVOID PROLONGED OR REPEATED CONTACT WITH SKIN."

M.A.C. (as CrO<sub>3</sub>) for an 8-hr. day: 0.1 mg./m.<sup>3</sup> 14

**Safety Classification:**

OSM: class 2

ICC: —

U.N.: poisonous (toxic)

**Fire and Explosion Hazard:** Emits highly toxic fumes when heated. An oxidant which reacts vigorously with reducing materials. 12

**Electrostatic Sensitivity:** —

**Use in Pyrotechnics:** Barium chromate is used as an oxidizing agent, and to impart a green color to a burning composition. 17

**Additional References:**

- 1) S. Peltier and C. Duval, Anal. Chim. Acta 1, 361 (1947)

**BARIUM NITRATE, Ba(NO<sub>3</sub>)<sub>2</sub>,  
(Nitrobarite)**

*Refs.*

Percent Oxygen: 36.73  
 Specification No.: MIL-R-162B  
 The specification covers six classes that differ in purity and granulation.  
 The following four classes are used in pyrotechnics:  
 Class 1, used in priming compositions (in two granulations);  
 2, used in photoflash compositions;  
 5, used in incendiary mixtures;  
 6, used in pyrotechnic compositions.

Molecular Weight: 261.38  
 Crystalline Form: cubic 1  
 Color: colorless 1  
 Density, g./ml.: (solid) 3.24 at 23°C 1  
 Coefficient of Thermal Expansion,  
 linear, -73° to +15°C:  $5 \times 10^{-6}$  44S30 sup  
 Heat of Formation, Kcal./mole at 298°K: -237.06 1, 9  
 Free Energy of Formation, Kcal./mole at 298°K: -190.0 9  
 Entropy, cal./deg./mole at 298°K: 51.1 9

**HEAT CONTENT AND ENTROPY OF Ba(NO<sub>3</sub>)<sub>2</sub>(c)  
(Base, crystals at 298.15°K; mol. wt., 261.38)**

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . .	3960	11.39	700 . . . .	13,460	38.14
500 . . . .	8410	21.30	800 . . . .	24,070	45.62
600 . . . .	13,240	30.10	850 . . . .	27,020	49.20

**Ba(NO<sub>3</sub>)<sub>2</sub>(c):**

Enthalpy:  $H_T - H_{298.15} = 30.05T + 17.85 \times 10^{-3}T^2 + 4.01 \times 10^5T^{-1} - 11,891$   
 (0.2 percent; 298° - 850°K)

Heat Capacity:  $C_p = 30.05 + 35.70 \times 10^{-3}T - 4.01 \times 10^5T^{-2}$

Melting Point: 868°K 7, 9  
 Heat of Fusion, Kcal./mole: 6 9  
 Boiling Point: decomposes 1  
 Transition Point: ———  
 Heat of Sublimation: ———  
 Heat Capacity, cal./deg./mole at 298°K: (solid) 36.1 9  
 See equation under table above

**Barium Nitrate, Ba(NO<sub>3</sub>)<sub>2</sub> (page 2)**

Decomposition Temperature:	555-600°C	Addnl. Ref. 1
For DTA see Refs. 33 and 47		
For TAG see Ref. 33		
Decomposition Products:	evolves NO <sub>2</sub> and O <sub>2</sub>	20V3
Vapor Pressure:	—	
X-Ray Crystallographic Data:		
System	Space Group	a
cubic	T <sub>h</sub>	8.11
		Molecules/Unit Cell
		4
Hygroscopicity:		
Gain in mg./g. at equilibrium at R.T.:	purified < 0.1 at 75% and 86% R.H. 0.6 at 93% R.H.	32
Solubility Data:		
In water (g./100 g.) at °C:	3.7 at 20°; 34.2 at 100°	1
In acids:	slightly soluble	
In alcohol, conc. nitric acid:	insoluble	
Health Hazard: Moderately poisonous. Irritates eyes, ears, nose, throat, and skin; produces dermatitis. When heated evolves toxic fumes. Produces gastrointestinal irritation.		93, 29, 12, 20, 50V7
M.A.C.	0.5	14
Safety Classifications:		
OSM: Class 1 when packed or shipped in original containers or equivalent.		
ICC:	Oxidizing material; yellow label	
Fire and Explosion Hazard: By itself the fire hazard is moderate. As a strong oxidizing agent it reacts vigorously when heated with reducing materials and may even result in detonation.		12
Electrostatic Sensitivity:	—	
Use in Pyrotechnics: Barium nitrate is used as an oxidizer, and to impart a green color to burning compositions.		17
Storage: Keep barium nitrate in a moisture-proof container in a dry place to prevent caking.		
Additional References:		
1) C.A. 49, 12932 (1955)		



BARIUM OXALATE, $\text{BaC}_2\text{O}_4$		Refs.
Specification No.:	JAN-B 560	
Molecular Weight:	225.38	
Crystalline Form:	—	
Color:	colorless	1
Density, g./ml.:	(solid) 2.658	1
Coefficient of Thermal Expansion:	—	
Heat of Formation, $\text{Kcal./mole}$ at		
$18^\circ\text{C}(\text{c}) \text{BaC}_2\text{O}_4$ :	-327.6	Addnl. Ref. 1
$25^\circ\text{C}(\text{c}) \text{BaC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ :	-363.7	1
$18^\circ\text{C}(\text{ppt.}) \text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ :	-397.57	1
$25^\circ\text{C} \text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ :	-470.1	2
$25^\circ\text{C} \text{BaC}_2\text{O}_4 \cdot 3.5\text{H}_2\text{O}$ :	-575.73	9
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	—	
Heat of Fusion:	—	
Boiling Point:	decomposes	
Heat of Vaporization:	—	
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature:	loses CO above $346^\circ\text{C}$	45
Decomposition Products:	$\text{CO} + \text{BaCO}_3$	
Vapor Pressure:	—	
X-Ray Crystallographic Data:	—	
Microscopicity:	—	
Solubility Data: In water, g./ml. solvent:	0.0093 at $18^\circ\text{C}$	1
	0.0228 at $100^\circ\text{C}$	
In acids, $\text{NH}_4\text{Cl}$ :	soluble	
In alcohol:	insoluble	
Health Hazard: Poisonous. Irritates eyes, nose, throat, and skin. Produces dermatitis.		12, 29
Safety Classifications:		
OSM:	not specifically mentioned	
ICC:	not specifically mentioned	
U.N.:	class 6 (II)—poisonous toxic substance	

**Barium Oxalate,  $\text{BaC}_2\text{O}_4$  (page 2)**

Fire and Explosion Hazard: Dangerous when heated to decomposition; emits toxic fumes. 12

Electrostatic Sensitivity: -----

Use in Pyrotechnics: As a retardant. Imparts some green color to burning compositions. 17

**Additional References:**

- 1) L. Médard, Mém. artillerie franç, 28, 467 (1954)

# BARIUM OXIDE, BaO

(Barium Monoxide, Baryta, Barium Protoxide, Calcined Baryta)

Specification No.:	-----	Refs.
Molecular Weight:	153.33	1, 11, 12, 29
Crystalline Form:	cubic or hexagonal	1
Color:	colorless	1
Density, g./ml.:	(solid) 5.72 (hex) 5.32	1
Coefficient of Thermal Expansion:	$3.0 \times 10^{-7}$	47
Heat of Formation, Kcal./mole at 298°K:	(c) -133.4	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(c) -126.3	1, 9

## Δ. HEAT AND FREE ENERGY OF FORMATION OF BaO(c)

(Mol. wt., 153.33)

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16 . . .	-133,500 (± 3000)	-126,500 (± 3500)
400 . . . .	-133,900	-124,000
500 . . . .	-133,000	-121,500
600 . . . .	-133,000	-119,500
648 . . . .	-132,500	-118,500
648 . . . .	-133,000	-118,500
700 . . . .	-132,500	-117,000
800 . . . .	-132,500	-115,000
900 . . . .	-132,500	-113,000
977 . . . .	-132,000	-111,000
977 . . . .	-134,500	-111,000
1000 . . . .	-134,500	-110,500
1100 . . . .	-134,000	-108,000
1200 . . . .	-134,000	-106,000
1300 . . . .	-133,500	-103,500
1400 . . . .	-132,500	-101,500
1500 . . . .	-133,000	-99,000
1600 . . . .	-133,000	-96,500
1700 . . . .	-132,500	-94,500
1800 . . . .	-132,500	-92,000
1900 . . . .	-132,000	-90,000
1911 . . . .	-132,000	-90,000
1911 . . . .	-167,500	-90,000
2000 . . . .	-167,000	-86,000

## Barium Oxide, BaO (page 2)

## Phase Changes of Metal

T.P. ( $\alpha \rightarrow \beta$ ), 648°K $\Delta H = 140$  cal./g.-atomM.P., 977°K;  $\Delta H = 2250$  cal./g.-atomB. P., 1911°K;  $\Delta H = 35,660$  cal./g.-atom

## Free Energy Equations:

Reaction	Range of Validity, °K	
1) $\text{Ba} (\alpha) + \frac{1}{2} \text{O}_2 (\text{g}) = \text{BaO} (\text{c})$	298.16 to 648	2
$\Delta F_T^\circ = -134,590 - 7.60T \log T + .87 (10^{-3}T^2) + .12 (10^5T^{-1}) + 45.76T$		
2) $\text{Ba} (\beta) + \frac{1}{2} \text{O}_2 (\text{g}) = \text{BaO} (\text{c})$	648 to 977	
$\Delta F_T^\circ = -134,140 - 3.34T \log T - .56 (10^{-3}T^2) + .42 (10^5T^{-1}) + 34.01T$		
3) $\text{Ba} (\text{l}) + \frac{1}{2} \text{O}_2 (\text{g}) = \text{BaO} (\text{c})$	977 to 1911	
$\Delta F_T^\circ = -135,900 - 2.19T \log T - .56 (10^{-3}T^2) + .42 (10^5T^{-1}) + 32.37T$		
4) $\text{Ba} (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g}) = \text{BaO} (\text{c})$	1911 to 2000	
$\Delta F_T^\circ = -176,400 - 8.61T \log T - .56 (10^{-3}T^2) + .42 (10^5T^{-1}) + 72.66T$		
Entropy, cal./deg./mole at 298°K:	(solid) 16.8 ± .03 (gas) 55.9 ± 5	1, 2, 9 3
See Tables b and c		
Melting Point:	2190°K (1917°C)	9
Heat of Fusion, Kcal./mole:	13.8 ± 2.0	24
Boiling Point:	about 2273°K (2000°C)	1
Transition Point:		
Heat of Sublimation, cal./mole:	90.0	24

## b. HEAT CONTENT AND ENTROPY OF BaO (c)

(Base, crystals at 298.15°K; mol. wt., 152.36)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	1170	3.36	1300 . . . . .	13,090	18.77
500 . . . . .	2380	6.07	1400 . . . . .	14,520	19.83
600 . . . . .	3660	8.40	1500 . . . . .	15,970	20.83
700 . . . . .	4980	10.43	1600 . . . . .	17,440	21.78
800 . . . . .	6300	12.20	1700 . . . . .	18,920	22.67
900 . . . . .	7620	13.75	1800 . . . . .	20,420	23.53
1000 . . . . .	8950	15.15	1900 . . . . .	21,930	24.35
1100 . . . . .	10,300	16.44	2000 . . . . .	23,450	25.13
1200 . . . . .	11,680	17.34			

## Barium Oxide, BaO (page 3)

## BaO (c):

Enthalpy:  $H_T - H_{298.15} = 11.79T + 0.94 \times 10^{-5}T^2 + 0.83 \times 10^{-8}T^3 - 3834$   
(0.5 percent; 298°–2000°K)

Heat Capacity:  $C_p = 11.79 + 1.88 \times 10^{-5}T - 0.88 \times 10^{-8}T^2$

c. HEAT CONTENT AND ENTROPY OF BaO (g)  
(Base, ideal gas at 298.15°K; mol. wt., 153.36)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	820	2.36	1000 . . . . .	5985	10.21
500 . . . . .	1650	4.21	1200 . . . . .	7750	11.82
600 . . . . .	2500	5.76	1400 . . . . .	9520	13.18
700 . . . . .	3365	7.10	1600 . . . . .	11,295	14.37
800 . . . . .	4235	8.26	1800 . . . . .	13,075	15.42
900 . . . . .	5110	9.29	2000 . . . . .	14,855	16.35

## BaO (g):

Enthalpy:  $H_T - H_{298.15} = 8.62T + 0.10 \times 10^{-5}T^2 + 0.67 \times 10^{-8}T^3 - 2804$   
(0.3 percent; 298°–2000°K)

Heat Capacity:  $C_p = 8.62 + 0.20 \times 10^{-5}T - 0.67 \times 10^{-8}T^2$

Decomposition Temperature: } When heated in air at 450°C, it combines  
Decomposition Products: } with O and forms BaO<sub>2</sub>. On further heating  
Vapor Pressure: } above 600°C, BaO<sub>2</sub> loses O and reforms BaO.  
For the range 900–1200°C:  $\log P = -(19400/T + 8.69)$

## X-Ray Crystallographic Data:

System	Space Group	$z$	Molecules/Unit Cell
cubic	O <sub>h</sub>	5.50	4

Hygroscopicity: Absorbs water with formation of Ba(OH)<sub>2</sub> with evolution of much heat

Absorbs moisture and CO<sub>2</sub> on exposure to air and forms BaCO<sub>3</sub>.

Caution: Keep in tightly closed container.

## Solubility Data: In water:

1.5 g./ml., decomposes  
90.8 g./100 ml. at 80°C

In dil. acids, alcohol:

soluble

In CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH:

slowly soluble

In NH<sub>3</sub>, acetic acid:

insoluble

Health Hazard: Poisonous. Irritates eyes, ears, nose, throat, and skin. Produces dermatitis. Gastrointestinal irritant:

M.A.C.:

0.5

**Barium Oxide, BaO (page 4)**

**Safety Classifications:**

OSM:	not specifically listed
ICC:	not specifically listed
U.N.:	classified under "Poisonous (toxic) substances."

**Fire and Explosion Hazard:** Produces considerable heat on contact with water or steam. Some hazard by chemical reaction. 12

**Electrostatic Sensitivity:** ———

**Use in Pyrotechnics:** BaO is a product of the burning of many barium compounds.

**Additional References:**

- 1) C.A. 52, 3446 (1958)

BARIUM PERCHLORATE, Ba(ClO <sub>4</sub> ) <sub>2</sub>				Refs
Percent Oxygen.	38.06			
Specification No.:	—			
Molecular Weight:	336.27			
Crystalline Form:	hexagonal			1
Color:	colorless			1
Density, g./ml.:	(solid) (3H <sub>2</sub> O) 2.74			29
Coefficient of Thermal Expansion:	—			
Heat of Formation, Kcal./mole at 298°K:	(c) -192.8			1, 9
Free Energy of Formation:	—			
Entropy, cal./deg./mole at 298.16°K:	57.7			36
Melting Point:	687°K (414°C)			1
	778°K (505°C)			65
Heat of Fusion:	—			
Boiling Point:	decomposes at 673°K (400°C)			12
	decomposes above 795°K (520°C)			Addnl. Ref. 1
Heat of Vaporization:	—			
Transition Points:	α to β at 557°K (284°C)			72
	β to γ at 633°K (360°C)			
Heat of Sublimation:	—			
Heat Content or Enthalpy:	—			
Heat Capacity:	—			
Decomposition Temperature:	vigorous decomposition at 534°C			47
Decomposition Products:	BaCl <sub>2</sub> and O <sub>2</sub>			Addnl. Ref. 1
For DTA and TGA see Ref. 33				
Vapor Pressure:	—			
X-Ray Crystallographic Data:				
System	Space Group	a	b	c Molecules/Unit Cell
rhombic	V <sub>h</sub> <sup>16</sup>	5.29	8.88	6.41 4
Hygroscopicity:	—			
Solubility Data: In water, g./100 ml.:	198.5 at 25°; very sol. hot			65
Solubility in Nonaqueous Solvents, at 25°C:				65, 77
Solvent	g./100 g. solvent			
acetone	124.7			
n-butyl alcohol	58.18			
ethyl acetate	112.9			
furfural (at 20°C)	43			
methyl alcohol	217.1			
n-propyl alcohol	75.65			

**Barium Perchlorate,  $\text{Ba}(\text{ClO}_4)_2$  (page 2)**

**Health Hazard:**  $\text{Ba}(\text{ClO}_4)_2$  is poisonous, irritates the eyes, nose, throat, and produces dermatitis. It may affect the central nervous system and kidneys. Its harmful effects are mainly due to the barium ion. Gastrointestinal irritant.

12, 26, 29,  
50V7

**Caution:** Avoid skin contact.

**M.A.C.:**

0.5

65  
14

**Safety Classifications:**

**OSM:** Class 1. Class 2 when not packed in original shipping container or equivalent.

**ICC:** Oxidizing material, yellow label. Listed under "Explosives and Other Dangerous Articles."

**Fire and Explosion Hazard:**  $\text{Ba}(\text{ClO}_4)_2$  is dangerous because it may be exploded by shock, heat, or chemical reaction. It forms explosive mixtures with carbonaceous material, S, powdered Mg, and Al. It emits highly toxic fumes when heated. Fires involving perchlorates alone may be fought with water.

12, 14

**Electrostatic Sensitivity:**

**Used in Pyrotechnics:**  $\text{Ba}(\text{ClO}_4)_2$  is used as an oxidizer, and to give a green color to burning compositions.

17

**Additional References:**

1) C.A. 51, 2439 (1957)



# BARIUM PEROXYDIDE, BaO<sub>2</sub>

(Barium Dioxide, Barium Superoxide, Barium Binoxide)

Percent Oxygen:	15.33	15.33
Specification No.:	JAN-P-153 (1)	1, 153
The specification covers one grade and three classes that differ in granulation.		
Molecular Weight:	169.36	
Crystalline Form:	powder	2
Color:	white to gray	3
Density, g./ml.:	(solid) 4.96	3
Coefficient of Thermal Expansion:	—	
Heat of Formation, kcal./mole at 298°K:	-150.5	1, 3
Free Energy of Formation:		

## HEAT AND FREE ENERGY OF FORMATION OF BaO<sub>2</sub> (c) (Mol. wt., 169.36)

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
233.16 . .	-153,000 (± 6000)	-140,500 (± 6000)
400 . . . .	-153,000	-123,500
500 . . . .	-152,500	-132,000
600 . . . .	-152,000	-128,000
64° . . . .	-152,000	-126,500
648 . . . .	-152,000	-126,500
700 . . . .	-152,000	-124,000
800 . . . .	-151,500	-120,500
900 . . . .	-151,000	-116,500
977 . . . .	-151,000	-113,500
977 . . . .	-153,000	-113,500
1000 . . . .	-153,000	-112,500
1100 . . . .	-152,500	-108,500
1200 . . . .	-152,500	-104,500
1300 . . . .	-152,000	-100,500
1400 . . . .	-151,500	-96,500
1500 . . . .	-151,000	-92,500

### Phase Changes of Metal

T.P. (α→β), 648°K;

Δ H = 140 cal./g.-atom

M.P., 977°K; Δ H = 2250 cal./g.-atom

Barium Peroxide, BaO<sub>2</sub> (page 2)

Free Energy Equations:

Reaction	Range of Validity, °K	
1) Ba(α) + O <sub>2</sub> (g) = BaO <sub>2</sub> (c) ΔF <sub>T</sub> <sup>o</sup> = -154,830 - 11.05T log T + .87 (10 <sup>-3</sup> T <sup>2</sup> ) + .42 (10 <sup>5</sup> T <sup>-1</sup> ) + 74.48T	298.16 to 648	2
2) Ba(β) + O <sub>2</sub> (g) = BaO <sub>2</sub> (c) ΔF <sub>T</sub> <sup>o</sup> = -154,380 - 679T log T - .56 (10 <sup>-3</sup> T <sup>2</sup> ) + .42 (10 <sup>5</sup> T <sup>-1</sup> ) + 62.73T	648 to 977	
3) Ba(l) + O <sub>2</sub> (g) = BaO <sub>2</sub> (c) ΔF <sub>T</sub> <sup>o</sup> = -156,140 - 5.64T log T - .56 (10 <sup>-3</sup> T <sup>2</sup> ) + .42 (10 <sup>5</sup> T <sup>-1</sup> ) + 61.09T	977 to 1500	
Entropy, cal./deg./mole at 298°K:	(c) 18.5	6
Melting Point:	723°K (450°C)	1
Heat of Fusion, Kcal./mole:	5.7	6
Boiling Point:	loses O at 1073°K (800°C) decomposes at 1110°K (837°C) at 1 atm.	1 8
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
See Ref. 2		
Decomposition Temperature, °C:	800	1
For DTA see Ref. 33		
Decomposition Products:	BaO + O	29 and Addnl Refs. 1, 2, 3

Vapor Pressure:

Dissociation Press.:	760 mm. at 795°C	Addnl. Ref. 1
Press. atm.	0.0149    0.0861    0.1855    0.945    1.220    1.534	42V7
Temp. °K	891.1    970.1    1010.1    1108.1    1126.1    1141.1	

X-Ray Crystallographic Data:

System	Space Group	a	c	Molecules/Unit Cell	
tetragonal	O <sub>h</sub> <sup>1</sup>	5.34	6.77		1
	D <sub>2h</sub> <sup>1</sup>	5.39	6.85	4	97V6

Hygroscopicity: Slowly decomposes in air and on contact with water. Combines with water to form BaO<sub>2</sub>·8H<sub>2</sub>O

Gain in mg./g. at R.T. after equil. was established in vac. desic.

Reagent Grade:

R.H.%	65	75	86	93	
24 hrs.	0.6	6.0	28.7	48.0	32
Equil.	1.0		73.1	126.0	

Solubility Data:	In cold water:	very soluble	1
	In hot water:	decomposes	
	In dilute acids:	soluble; with decomposition forming H <sub>2</sub> O <sub>2</sub>	
	In acetone:	insoluble	

**Barium Peroxide, BaO<sub>2</sub> (page 3)**

Health Hazard: BaO<sub>2</sub> is poisonous. It irritates the eyes, nose, and throat, and produces dermatitis. Gastrointestinal irritant. 29, 12, 50V7

M.A.C.: 0.5 14

**Safety Classifications:**

OSM: Class 1. Class 2 when not packed in original containers or equivalent.

ICC: Oxidizing material; yellow label.

Fire and Explosion Hazard: As an oxidizer it is dangerous when heated with reducing material; may result in detonation. 12

**Electrostatic Sensitivity:** ———

Use in Pyrotechnics: BaO<sub>2</sub> is used as an oxidizer and to impart a green color to burning compositions. It is used in igniter and tracer compositions. 17

**Additional References:**

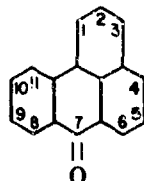
- 1) "The Decomposition of Barium Peroxide and the Reactivity of the Resulting Barium Oxide," J. A. Hedvall, *Zeit. anorg. Chem.* 104, 163 (1918); *J. Chem. Soc. Abstracts* 1919 ii, 26
- 2) "Kinetics of the dissociation of Ba and Ca peroxides," M. M. Pavlyuchenko and Yu S. Rubinchik, *C.A.* 52, 19362 (1958)
- 3) "Heating curves for the hydrates of the peroxides of the Group II metals," I. I. Vol'nov, *C.A.* 52, 19384 (1958)

# BENZANTHRONE, C<sub>17</sub>H<sub>10</sub>O

(7-oxo-7-benz(d,e)anthraquinone, 7-H-benz(d,e)anthracene-7-one, 7-meso-benzanthrone, Benzan B, Research Vat Golden Yellow GK)

Refs.

Structural Formula:



Specification No.:	MIL-B-50074
The specification requires:	purity—minimum 77% water—maximum 1%
Molecular Weight:	230.25
Crystalline Form:	
From alcohol or benzene:	orthorhombic
From nitrobenzene:	needles
Color:	pale yellow
Density, g./ml.:	(solid) 1.371
Coefficient of Thermal Expansion:	—
Heat of Formation:	—
Free Energy:	—
Entropy:	—
Melting Point:	447°K (174°C) 423.1°K (173.1°C)
Heat of Fusion:	—
Boiling Point:	—
Transition Point:	—
Heat of Sublimation:	—
Heat Content or Enthalpy:	—
Heat Capacity:	—
Decomposition Temperature, °C:	about 426° (see below)
For DTA and TGA see Refs. 80 and 81	
Decomposition Products:	—
Vapor Pressure:	

Addnl. Ref. 3

Addnl. Ref. 3

Addnl. Ref. 1

Press. mm.	1	10	40	100	200
Temp. °C	225.0	297.2	350.0	390	428.5 with decompn

1

**Benzanthrone (page 2)****X-Ray Crystallographic Data:**

System	Space Group	a	b	c	Molecules/ Unit Cell
orthorhombic	D <sub>2</sub> <sup>h</sup>	14.57	15.00	5.07	4

For bond lengths see Addnl. Ref. 2

18V III,  
Addnl. Ref. 3**Hygroscopicity:**

Solubility Data: at 20°C per 100 g. solvent,

glacial acetic acid: 0.52

benzene: 0.61

chlorobenzene: 2.05

in tetrachlorethane: soluble

In con. H<sub>2</sub>SO<sub>4</sub>: soluble, giving an orange-red color with an olive-green fluorescence

29

89V14

88V7 II

In toluene: soluble

Health Hazard: Some, as indicated by the spec. requirement that "each container shall be conspicuously labeled: 'CAUTION—AVOID SKIN CONTACT; USE WITH ADEQUATE VENTILATION.'"

Fire and Explosion Hazard:

slight when heated;  
emits smoke

12

**Safety Classifications:**

OSM: not listed

ICC: not listed

**Electrostatic Sensitivity:**

Use in Pyrotechnics: To produce a yellow color in smoke grenades.

**Additional References:**

- 1) "Freezing Point and Purity Data for Some Organic Compounds," C. R. Witschonke, *Anal. Chem.* 26, 563 (1954)
- 2) "Calculated Bond Lengths in Some Cyclic Compounds. Part II. Benzanthrone, Acedianthrone, and Flavanthrone," T. H. Goodwin, *J. Chem. Soc.* 1955, 1689
- 3) "Cell Dimensions and Space Groups of Some Carbocyclic Compounds," H. C. Boyd et al., *Acta Cryst.* 7, 142 (1954)

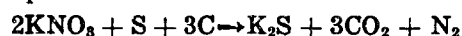
## BLACK POWDER

### (Gunpowder)

Black powder is an intimate mechanical mixture of potassium or sodium nitrate, charcoal, and sulfur. Willow or alder charcoal and flour of sulfur and 2-3% of water are well mixed in a tumbling barrel. This mixture is transferred to a wheel mill and the desired amount of crystalline potassium nitrate and several percent of water are added. The mill is run for several hours to obtain a uniform mixture. During mixing the mixture is kept damp by the addition of water. The mixture is pressed at about 6000 psi and then broken up by passing between rolls. Broken pieces are screened into sizes and material of undesired size is reconsolidated and passed through rolls and screened. Material of acceptable size is then thoroughly dried in hot air ovens at about 60°C. The material may be polished before drying by rotating it in a tumbling barrel. After tumbling, the black powder is sieved and the fines removed.

Black powder is sensitive to friction, heat, and impact, and is very dangerous to handle. It absorbs moisture and deteriorates rapidly. If kept dry, it will retain its properties indefinitely. Combustible materials that have absorbed liquors leached from black powder are a severe fire hazard and may become explosive. Every safety precaution should be taken in black powder manufacture and operations.

Black powder has a composition close to the stoichiometric proportions needed to satisfy the equation:



In practice, the proportions may be varied slightly.

Formula (specification):

KNO<sub>3</sub>, 74.0%  
S, 10.4%  
charcoal, 15.6%

Specification No.:

JAN-P-223A

(all seven grades listed in the specification are used in pyrotechnics)

Crystalline Form:

mechanical mixture

Color:

black

Density, g./ml.:

approx. 1.6, variable depending mainly on conditions of preparation

Decomposition Temperature: Exothermal preignition reaction starts at about 250°C and culminates at approximately 300°C (DTA and TGA curves).

Decomposition Products:

— —

Hygroscopicity: Black powder is appreciably hygroscopic and is prepared and kept under conditions of low humidity so that its properties will not be adversely affected.

Temp. °C	R.H. %	Gain %
26	75	0.75
25	90	1.91
30	90	2.51

Refs.

13, 50V6

14, 13

13

Addnl. Ref. 4

13

# Black Powder (page 2)

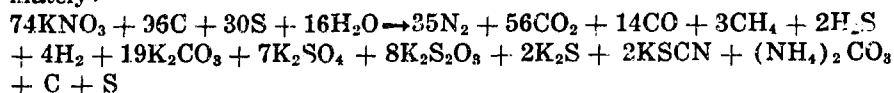
## Explosion Data:

Specific Volume at S.T.P., l./kg.: 285 (H<sub>2</sub>O gas)  
 Explosion Temperature, °C: 2770  
 Heat of Explosion, Kcal./kg.: 685 (H<sub>2</sub>O liquid)  
 Characteristic Product (V<sub>0</sub>Q): 195,200

Addnl. Ref. 5

The equation for the burning of black powder has been given as approximately:

50V6



For other equations see Ref. 54V2

Health Hazard: none mentioned

## Safety Classifications:

OSM: Class 9 (in charges or containers)  
 ICC: Class A explosive, not accepted for railway express. Black powder igniters with empty cartridge bags, classified class C explosives.

Fire and Explosion Hazard: Black powder can be detonated by friction, heat, and impact.

14

Electrostatic Sensitivity: unconfined > 12.5 joules  
 energy required to ignition: confined 0.8 joules

Addnl. Ref. 6

Impact Sensitivity, 2 kg. weight falling on 16 mg. sample:

Bureau of Mines Apparatus, cm. 32 (10% Point)  
 P.A. Apparatus, in. 16 (10% Point)

Following data on this page from 13

Initiating Efficiency (min. wt. in grams required to initiate B.P.):

Igniter Composition K-31: 2.0  
 Igniter Composition K-29: 2.3

## Friction Pendulum Test:

Steel shoe: snaps  
 Fibre shoe: unaffected

Temperature Test: (0.02 g. sample in No. 6 copper detonating cap)

Seconds	Temp. °C
0.1 (no cap used)	510
1	490
5	427 ignited
10	356

## 75% International Heat Test:

Loss in 48 hrs., weight %: 0.31

Vacuum Stability Tests, cc./hrs. on 5 g. sample: 100°C, 0.5  
 120°C, 0.9

Sand Test, with 200 g. bomb and 0.4 g. sample of black powder:

Grams sand crushed to pass 40-mesh screen: 8  
 Sensitivity: tetryl, 0.25 g.

Ballistic Mortar, % of TNT: 50

**Black Powder (page 3)**

Trauzl Test, % of TNT:	10
Detonation Rate, meters/sec. at density 1.6:	400
Heat of Explosion, cal./g.:	684
Gas Volume on Explosion, cc./g.	271
Method of Loading:	1) loose (granulated) 2) pressed

Loading Density, g./cc. in thousands of psi:

psi	25	50	60	65	70	75
Density	1.74	1.84	1.86	1.87	1.88	1.89

Method of Storage: dry

100° Vacuum Stability Test, cc. gas/40 hrs. from a 5 g. sample:

Initial value:	0.5
After 2 years at 65°C:	0.86
After 2 years at 65°C and 75% R.H.:	1.46

Compatibility with metals:

- Dry—compatible with all metals when moisture content is less than 0.2%.  
Wet—attacks all common metals except stainless steel.

Destruction:

Black powder may be completely destroyed by leaching or washing with large quantities of water and disposing of the washings separately from the residue.

Use in Pyrotechnics: Black powder is used as an igniter powder, and in time fuzes (fuzes), fireworks, rockets, Roman candles, and firecrackers.

**Additional References:**

- 1) "Initiation, Burning and Thermal Decomposition of Gunpowder," J. Blackwood and F. Bowden, *Proc. Roy. Soc.* 213, 285 (1952)
- 2) "Chemistry of Powder and Explosives," T. L. Davis, John Wiley & Sons, Inc., New York (1943)
- 3) Refs. 52V4 and 54V2
- 4) "A Thermoanalytical Study of the Ignition and Combustion of Black Powder," C. Campbell and G. Weingarten, *Trans. Faraday Soc.* 55, 2221 (1959)
- 5) "Explosives," H. Brunswig, John Wiley & Sons, Inc., New York (1912)
- 6) "Sensitivity of Explosives to Initiation by Electrostatic Discharges," F. W. Brown et al., U.S. Dept. of Interior, Bureau of Mines, R.I. 3852 (1946)

14



# **BORON, B**

		<i>Refs.</i>
Specification No.:	PAPD-451	
Molecular Weight:	10.82	
Crystalline Form:	monoclinic crystals or amorphous powder	1
Color:	yellow or brown	1
Density, g./ml.:	(c) 2.34 (amor.) 2.37 2.35	1A 31A
Coefficient of Thermal Expansion, linear, 20-750°C:	$17.4 \times 10^{-6}$ per °C	27
Heat of Formation, Kcal./mole at 298°K:	(gas) 97.2	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 86.7	1, 9
Entropy, Kcal./mole at 298°K:	(c) 1.40 (gas-monatomic) 36.65	5 5
See Table a		
Melting Point:	2313°K (2037 ± 37°C)	31A
Heat of Fusion, cal./mole:	5300	5
Boiling Point:	4198°K (39275°C)	31A
Heat of Vaporization, cal./mole:	128,000	5
Transition Point:	—	
Heat of Sublimation, cal./mole at 298°K:	141,000	5
Heat Content or Enthalpy, cal./mole at 298°K:	292	5
See Tables a and b		
Heat Capacity, cal./deg./mole at 298°K:	(solid) 2.63 (liquid) 7.5 (gas) 4.97	5, 9

See equations under Tables a and b

## **a. HEAT CONTENT AND ENTROPY OF B(c, l)** (Base, crystals at 298.15°K; atomic wt. 10.82)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	310	0.89	1700 . . . . .	7765	8.61
500 . . . . .	690	1.73	1800 . . . . .	8460	9.00
600 . . . . .	1120	2.52	1900 . . . . .	9165	9.38
700 . . . . .	1600	3.26	2000 . . . . .	9880	9.75
800 . . . . .	2120	3.95	2100 . . . . .	10,605	10.10
900 . . . . .	2670	4.60	2200 . . . . .	11,340	10.45
1000 . . . . .	3245	5.20	2300 (c) . . .	12,080	10.78
1100 . . . . .	3845	5.78	2300 (l) . . .	17,380	13.03
1200 . . . . .	4465	6.31	2400 . . . . .	18,130	13.40
1300 . . . . .	5100	6.82	2600 . . . . .	19,630	14.03
1400 . . . . .	5750	7.30	2800 . . . . .	21,130	14.55
1500 . . . . .	6410	7.76	3000 . . . . .	22,630	15.07
1600 . . . . .	7080	8.19			

Boron, B (page 2)

B(c):

Enthalpy:  $H_T - H_{298.15} = 4.13T + 0.83 \times 10^{-5}T^2 + 1.76 \times 10^5T^{-1} - 1895$   
(2.1 percent; 298° - 2300°K)

Heat Capacity:  $C_p = 4.13 + 1.66 \times 10^{-5}T - 1.76 \times 10^5T^{-2}$

B(l):

Enthalpy:  $H_T - H_{298.15} = 7.50T + 130$  (0.1 percent; 2300° - 3000°K)

b. HEAT CONTENT AND ENTROPY OF B(amor.)  
(Base, amorphous substance at 298.15°K; atomic wt., 10.82)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	350	1.00	900 . . . . .	3160	5.40
500 . . . . .	785	1.97	1000 . . . . .	3840	6.12
600 . . . . .	1295	2.90	1100 . . . . .	4535	6.78
700 . . . . .	1870	3.78	1200 . . . . .	5255	7.40
800 . . . . .	2500	4.62			

B(amor.):

Enthalpy:  $H_T - H_{298.15} = 3.34T + 1.98 \times 10^{-5}T^2 + 1.48 \times 10^5T^{-1} - 1668$   
(1.1 percent; 298° - 1200°K)

Heat Capacity:  $C_p = 3.34 + 3.96 \times 10^{-5}T - 1.48 \times 10^5T^{-2}$

c. HEAT CAPACITY OF B  
(Solid to 2300°K; liquid from 2300° to 3000°K)

T, °K	$C_p$ (cal./deg./mole)
298	2.63
400	3.45
800	5.35
1200	6.27
1600	6.78
2000	7.20
2200	7.40
2300-3000	7.50

Decomposition Temperature: \_\_\_\_\_

Decomposition Products: \_\_\_\_\_

Vapor Pressure: \_\_\_\_\_

Press. mm.	$10^{-8}$	$10^{-6}$	$10^{-4}$	$10^{-2}$	1	$10^2$	760	M.P.
Temp. °K	1650	1850	2100	2430	2980	3730	4200	2300

**Boron, B (page 3)**

**X-Ray Crystallographic Data:**

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>c</i>	<i>Molecules/Unit Cell</i>	
tetragonal	$D_{2d}^8$ or $C_{4v}$	8.73 Å	5.03	50	18
hexagonal		11.98	9.54	180	

See also Ref. 44S13 sup

**Hygroscopicity:**

<b>Solubility Data:</b> In water:	insoluble (slightly soluble when freshly prepared)	1, 29
In $HNO_3$ , $H_2SO_4$ :	soluble	
In alc., eth., alk.:	insoluble	

**Health Hazard:** Boron is not highly toxic but it is a cumulative poison which affects the central nervous system. 12, 25

**Safety Classification:**

OSM: Class 2 when not packed in original containers or equivalent.

**Fire and Explosion Hazard:** Boron dust is dangerous as it can ignite on contact with air and explode. It reacts with oxidizing agents and is a dangerous fire and explosion hazard. It burns with intense heat. In the presence of moisture hydrogen may be evolved. Therefore B should be stored in a dry atmosphere and in a properly vented building. Use only nonsparking tools around B. To fight a fire use no water; use powdered graphite, dolomite, salt, or other inert material. At about 600° it ignites and burns with a brilliant green flame. 12, 14, 16

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:** Boron is used as a component of non-gaseous fuze powders.

**Additional References:**

- 1) "Boron," J. A. Kohn et al., eds., Plenum Press, Inc., New York (1960). Proceedings of the Conference on Boron, sponsored by the Institute for Exploratory Research, The U.S. Army Signal Research and Development Laboratory, Fort Monmouth, N.J.

# CALCIUM, Ca

		Refs.
Specification No.:	12056A (tech.)	
Molecular Weight:	40.08	
Crystalline Form:	cubic	1
Color:	silvery white when first cut; tarnishes to blue-grey on exposure to air	29
Density, g./ml.:	(solid) 1.55	1
Coefficient of Thermal Expansion, linear, 0-300°:	$22 \times 10^{-6}$	36
	cubic, 0-21°: $717 \times 10^{-6}$	
Heat of Formation, Kcal./mole at 298°K:	(gas) 42.200	5
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 34.138	5
Entropy, cal./deg./mole, at 298°K:	(c) $9.95 \pm .10$	3, 5
	(gas) 36.99	5
See Tables a, b, and c		
Melting Point:	1123°K (850°C)	4, 5
Heat of Fusion, cal./mole:	$2070 \pm 80$	4, 5
Boiling Point:	1765°K (1492°C)	5
Heat of Vaporization, cal./mole:	35,840	5
Transition Point:	$\alpha$ to $\beta$ 713°K (440°C)	4, 5
Heat of Transition, cal./mole:	270	4
Heat of Sublimation, cal./mole, at 298°K:	42,200	5
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 1380	5
See Tables a, b, and c		
Heat Capacity, cal./deg./mole at 298°K:	(solid) 6.30	4, 5
	(liquid) 7.40	
	(gas) 4.97	

## 2. HEAT CONTENT AND ENTROPY OF Ca(c, l) (Base, $\alpha$ -crystals at 298.15°K; atomic wt., 40.08)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	660	1.90	1123 ( $\beta$ ) . . .	6825	10.39
500 . . . . .	1340	3.42	1123 (l) . . .	8895	12.23
600 . . . . .	2055	4.72	1200 . . . . .	9465	12.72
700 . . . . .	2800	5.87	1300 . . . . .	10,205	13.31
713 ( $\alpha$ ) . . .	2300	6.01	1400 . . . . .	10,945	13.86
713 ( $\beta$ ) . . .	3170	6.39	1500 . . . . .	11,685	14.37
800 . . . . .	3850	7.23	1600 . . . . .	12,425	14.85
900 . . . . .	4690	8.28	1700 . . . . .	13,165	15.30
1000 . . . . .	5605	9.24	1800 . . . . .	13,905	15.72
1100 . . . . .	6590	10.18			

Calcium, Ca (page 2)

Ca( $\alpha$ ):

Enthalpy:  $H_T - H_{298.15} = 5.25T + 1.72 \times 10^{-5}T^2 - 1718$  (0.3 percent; 298° - 713°K)

Heat Capacity:  $C_p = 5.25 + 3.44 \times 10^{-5}T$

Ca( $\beta$ ):

Enthalpy:  $H_T - H_{298.15} = 2.58T + 3.40 \times 10^{-5}T^2 - 472$  (0.1 percent; 713° - 1123°K)

Heat Capacity:  $C_p = 2.68 + 6.80 \times 10^{-5}T$

Ca(l):

Enthalpy:  $H_T - H_{298.15} = 7.40T + 585$  (0.1 percent; 1123° - 1800°K)

D. HEAT CONTENT AND ENTROPY OF Ca(g)  
(Base, ideal gas at 298.15°K; atomic wt., 40.08)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	505	1.46	1900 . . . . .	7965	9.21
500 . . . . .	1005	2.57	2000 . . . . .	8465	9.46
600 . . . . .	1500	3.48	2200 . . . . .	9470	9.94
700 . . . . .	1995	4.24	2400 . . . . .	10,490	10.39
800 . . . . .	2495	4.90	2600 . . . . .	11,535	10.80
900 . . . . .	2990	5.49	2800 . . . . .	12,615	11.20
1000 . . . . .	3490	6.01	3000 . . . . .	13,745	11.59
1100 . . . . .	3985	6.49	3500 . . . . .	16,880	12.56
1200 . . . . .	4480	6.92	4000 . . . . .	20,670	13.57
1300 . . . . .	4980	7.32	4500 . . . . .	25,250	14.64
1400 . . . . .	5475	7.69	5000 . . . . .	30,685	15.79
1500 . . . . .	5975	8.03	5500 . . . . .	43,870	18.18
1600 . . . . .	6470	8.35	7000 . . . . .	59,365	20.57
1700 . . . . .	6970	8.65	8000 . . . . .	76,140	22.81
1800 . . . . .	7465	8.94			

Ca(g):

Enthalpy:  $H_T - H_{298.15} = 4.97T - 1482$  (0.1 percent; 298° - 2500°K)

Calcium, Ca (page 3)

c. HEAT CAPACITY OF Ca

Solid I from 298° - 713°K Solid II from 713° - 1123°K		Liquid from 1123° - 1765°K Gas (mon) from 1765° - 3000°K	
T, °K	C <sub>p</sub> (cal./deg./mole)	T, °K	C <sub>p</sub> (cal./deg./mole)
293	6.30	1200 to	
400	6.64	1700	7.40
600	7.21	1800	4.99
700	7.64	2200	5.06
800	8.00	2600	5.30
900	8.70	3000	5.80
1000	9.49		
1100	10.18		

Decomposition Temperature:

Decomposition Products:

DTA

Vapor Pressure:

Press. mm.	10	40	100	400	760	M.P.
Temp. °C	923	1111	1207	1388	1487	851

X-Ray Crystallographic Data:

System	Space Group	a	Atoms/Unit Cell
cubic	O <sub>h</sub> <sup>5</sup>	5.56	4

Hygroscopicity: Reacts with water (much slower than does sodium) to form Ca(OH)<sub>2</sub> and hydrogen.

Solubility Data: In water:

reacts to form Ca(OH)<sub>2</sub> and hydrogen

In acids:

soluble

In alcohol:

slightly soluble, with which it reacts slowly

In benzene, liquid NH<sub>3</sub>, kerosene:

insoluble

Health Hazard:

caustic to all tissues

Safety Classifications:

OSM:

not listed

ICC:

not listed

U.N.:

not listed

Fire and Explosion Hazard. The powdered metal exposed to air is a dangerous fire hazard. It burns with intense heat and a crimson flame. When compounded with oxidizing agents the powdered metal is both a dangerous fire and explosion hazard. It is a strong reducing agent. Contact with alkali hydroxides or carbonates may cause detonation. Precautions should be taken to prevent water from contacting the material. Store and process it only in rooms or buildings adequately vented at the highest point to prevent

**Calcium, Ca (page 4)**

accumulation of evolved hydrogen gas which results from the reaction of powdered metal and moisture. In the repair or maintenance of buildings or equipment, powder or dust should be removed and non-sparking tools used.  $\text{CCl}_4$  should not be used near calcium as an explosion may occur.

**Addnl. Ref. 2**

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:** As a fuel and to impart a crimson color to burning compositions.

**Additional References:**

- 1) Ref. 94
- 2) C.A. 37, 2578 (1943)

**CALCIUM CARBONATE,  $\text{CaCO}_3$**   
 (Marble, Precipitated Chalk, Whiting, White Chalk, Prepared Chalk,  
 Calcite, Drop Chalk, Paris White, English White, Iceland Spar)

Specification No.:	JAN-C-293	Refs.
Molecular Weight:	100.09	1, 11, 29
Crystalline Form:	(aragonite) rhombic (calcite) hexagonal	1
Color:	colorless	1
Density, g./ml.:	(aragonite) 2.93 (calcite) 2.711	1
Coefficient of Thermal Expansion,		
cubical, marble:	$0.3 - 0.6 \times 10^{-4}$	1
Iceland Spar, 50-60°C:	$0.1447 \times 10^{-4}$	1
calcite, linear — parallel to axis, 0-85°C:	$25.14 \times 10^{-6}$	1
perpendicular to axis, 0-85°C:	$5.88 \times 10^{-6}$	
Heat of Formation, Kcal./mole at 298°K:	aragonite (c) -288.49 calcite (c) -288.45	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	aragonite (c) -269.53 calcite (c) -269.78	1, 9
Entropy, cal./deg./mole at 298°K:	(aragonite) $22.2 \pm 0.3$ (calcite) $22.2 \pm 0.2$	3 3
See Tables a and b		
Melting Point:	(aragonite) about 1098°K (825°C)	1
(at 102.5 atm.)	(calcite) 1612°K (1339°C)	
Heat of Fusion, 15°g. cal./mole:	12,700	7
Boiling Point:	—	
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	see below	

**a. HEAT CONTENT AND ENTROPY OF  $\text{CaCO}_3$  (CALCITE)**  
 (Base, crystals at 298.15°K; mol. wt., 100.09)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	2220	6.38	900	15,530	27.31
500	4610	11.71	1000	18,430	30.70
600	7200	16.43	1100	21,450	33.58
700	9890	20.57	1200	24,550	36.27
800	12,600	24.27			



Calcium Carbonate (page 2)

CaCO<sub>3</sub> (calcite):

Enthalpy:  $H_T - H_{298.15} = 24.98T + 2.62 \times 10^{-5}T^2 + 6.20 \times 10^{-8}T^{-1} - 9760$   
(0.3 percent; 298° - 1200°K)

Heat Capacity:  $C_p = 24.98 + 5.24 \times 10^{-5}T - 6.20 \times 10^{-8}T^{-2}$

b. HEAT CONTENT AND ENTROPY OF CaCO<sub>3</sub> (ARAGONITE)  
(Base, crystals at 298.15°K; mol. wt., 100.09)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350 . . . . .	1050	3.24	500 . . . . .	1400	11.27
400 . . . . .	2130	6.13	550 . . . . .	5650	13.58
450 . . . . .	3260	8.79	600 . . . . .	6900	15.75

CaCO<sub>3</sub> (aragonite):

Enthalpy:  $H_T - H_{298.15} = 20.13T + 5.12 \times 10^{-5}T^2 + 3.34 \times 10^{-8}T^{-1} - 7577$   
(0.1 percent; 298° - 600°K)

Heat Capacity:  $C_p = 20.13 + 20.24 \times 10^{-5}T - 3.34 \times 10^{-8}T^{-2}$

Heat Capacity, cal./deg./mole:

(aragonite) 19.42  
(calcite) 19.57

Decomposition Temperature:

about 825°C

S. Peltier and C. Duval, Anal. Chim. Acta 1, 345-347 (1947) states that  
CaCO<sub>3</sub> loses CO<sub>2</sub> at 660°C and changes to CaO. See also Addnl. Ref. 1.

Decomposition Products:

CaO + CO<sub>2</sub>

For Dissociation Pressure see Ref. 54V3

$\log P_{atm.} = 11,355/T - 5.388 \log T + 26.238$

Vapor Pressure:

X-Ray Crystallographic Data:

	System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell
aragonite:	rhomb.	V <sub>h</sub> <sup>16</sup>	4.94	7.94	5.72		4
calcite:	rhbdr.	D <sub>3d</sub> <sup>14</sup>	6.361			$\alpha = 46^\circ 6'$	2

Hygroscopicity:

Solubility Data: In water:

insoluble

In water saturated with CO<sub>2</sub>:

slightly soluble

In dilute acids:

soluble with evolution of  
CO<sub>2</sub>

Health Hazard: Large doses may cause constipation

**Calcium Carbonate (page 3)**

**Safety Classifications:**

OSM:	not listed
ICC:	not listed
U.N.:	not listed

<b>Fire and Explosion Hazard:</b>	none
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**Electrostatic Sensitivity:** \_\_\_\_\_

**Use in Pyrotechnics:**  $\text{CaCO}_3$  is used as a retardant and antacid. It imparts a yellow-red color to burning compositions. 1

**Additional References:**

- 1) "Differential Thermal-Analysis Studies of Ceramic Materials: 1, Characteristic Heat Effects of Some Carbonates", R. M. Gruver, J. Am. Ceram. Soc. 33, 96 (1950)

**CALCIUM NITRATE,  $\text{Ca}(\text{NO}_3)_2$**   
(Lime Saltpeter, Lime Nitrate, Nitro Calcite, Norway Saltpeter)

*Refs.*  
1, 11, 16

Percent Oxygen:	58.50	
Specification No.:	none	
Molecular Weight:	164.10	
Crystalline Form:	cubic	1
Color:	colorless	1
Density, g./ml.:	(solid) 2.36	1
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	(c) -224.0	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(c) -177.34	1, 9
Entropy, cal./deg./mole at 298°K:	46.2	1, 4, 9
See table below		
Melting Point:	834°K (561°C)	7, 9
Heat of Fusion, Kcal./mole:	5.1	9
Boiling Point:	decomposes	1
Heat of Vaporization:	—	
Transition Point:	—	
Heat of Sublimation:	—	

**HEAT CONTENT AND ENTROPY OF  $\text{Ca}(\text{NO}_3)_2(\text{c})$**

(Base, crystals at 298.15°K; mol. wt., 164.10)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	3960	11.42	700 . . . . .	18,410	38.01
500 . . . . .	8340	21.15	800 . . . . .	23,970	45.43
600 . . . . .	13,150	29.91			

**$\text{Ca}(\text{NO}_3)_2(\text{c})$ :**

Enthalpy:  $H_T - H_{298.15} = 29.37T + 18.40 \times 10^{-5}T^2 + 4.13 \times 10^{-7}T^3 - 11,778$  (0.3 percent; 298° - 800°K)

Heat Capacity:  $C_p = 29.37 + 36.80 \times 10^{-5}T - 4.13 \times 10^{-7}T^2$

Heat Capacity, cal./deg./mole: (solid) 35.69

See also equation immediately above

9

Decomposition Temperature: 480-500°C

Decomposition Products: —

For DTA and TGA see Refs. 33 and 47

Vapor Pressure: —

Addnl. Ref. 1

**Calcium Nitrate,  $\text{Ca}(\text{NO}_3)_2$  (page 2)**

**X-Ray Crystallographic Data:**

System	Space Group	$a$	Molecules/Unit Cell	
cubic	$T_h^h$	7.60	4	1, 97V7

**Hygroscopicity:** Deliquesces in moist air. Keep in tightly closed container.

29

**Solubility Data:** In water, g./100 ml. at °C: 102 at 0°, 341 at 25°, 376 at 100°

In acids: very soluble

29

In ethyl, acetate, and alcohol: soluble

**Health Hazard:** Large amounts taken internally are poisonous.

12

**Safety Classifications:**

OSM: Class 1

ICC: Listed under "Explosives and Other Dangerous Articles." Oxidizing material; yellow label.

**Fire and Explosion Hazard:**  $\text{Ca}(\text{NO}_3)_2$  may explode when shocked, or by heat, flame, or chemical reaction. It is a strong oxidizing agent and reacts vigorously with oxidizable materials.  $\text{Ca}(\text{NO}_3)_2$  emits toxic fumes on decomposition.

12

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:**  $\text{Ca}(\text{NO}_3)_2$  is used as an oxidizer and to impart a yellow-red color to burning compositions.

1

**Additional References:**

1) C.A. 49, 12932 (1955)

**CALCIUM OXALATE,  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$**   
(Monohydrate)

Specification No.: JAN-C-628  
Molecular Weight: 146.12  
Crystalline Form: monoclinic  
Color: colorless  
Density, g./ml.: (solid) 2.2  
Coefficient of Thermal Expansion: —  
Heat of Formation, Kcal./mole at 298°K: -399.1  
Free Energy of Formation, Kcal./mole at 298°K: -340.6  
Entropy, cal./deg./mole at 298°K: 37.28  
Melting Point: loses  $\text{H}_2\text{O}$  at 473° K (200°C)  
Heat of Fusion: —  
Boiling Point: —  
Transition Point: —  
Heat of Sublimation: —  
Heat Content or Enthalpy: —  
Heat Capacity, cal./deg./mole: (solid) 36.40  
Decomposition Temperature: TGA

See pyrolysis curve below  
Decomposition Products: Calcium carbonate, calcium oxide.  
See pyrolysis curve below

Dissociation Pressure for  $\text{CaC}_2\text{O}_4$ :

T°C	P <sub>mm.</sub>	T°C	P <sub>mm.</sub>
378	8.2	410	250.0
388	80.0	416	587.0
403	134.0	418	684.0

X-Ray Crystallographic Data:

System	Space Group	a	c	Molecules/Unit Cell
2½ $\text{H}_2\text{O}$ tetragonal	$\text{C}_{4h}^1$	12.302	7.381	
3 $\text{H}_2\text{O}$	$\text{C}_{4h}^1$	12.375	7.377	4

Hygroscopicity: —

Solubility Data:

In water, acetic acid, and alcohol: insoluble  
In acids: soluble

Health Hazard: Corrosive and produces local irritation. Has a caustic effect on mouth, esophagus, and stomach. Can cause severe damage to kidneys.

*Refs.*

1, 5

1

1

1

1

1, 9

1, 29

9

Addnl. Refs.  
1, 2, 3, 4, 5

91

91

18V2

85

1

12

**Calcium Oxalate,  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (page 2)**

**Safety Classifications:**

OSM:

not listed

ICC:

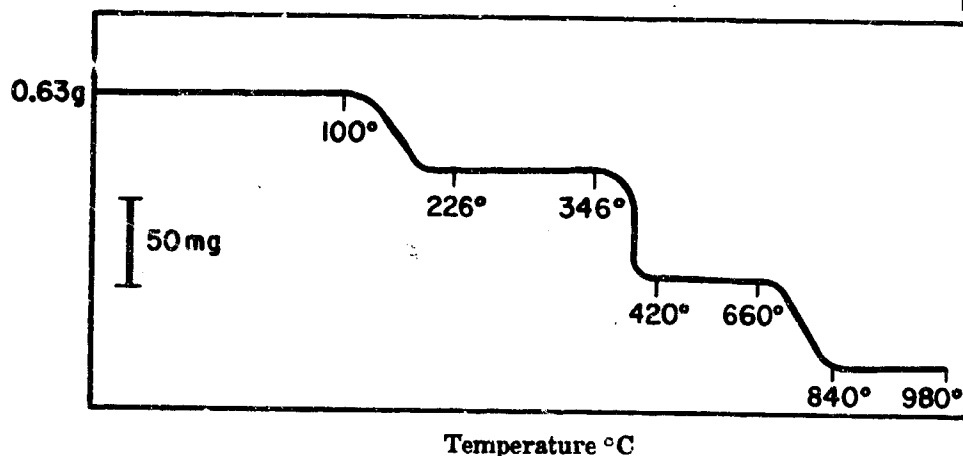
not listed

**Fire and Explosion Hazard:** Can be dangerous when heated to decomposition because of toxic fumes. 12

**Electrostatic Sensitivity:** —

**Pyrolysis Curves of Calcium Oxalate, Carbonate, and Oxide**

Addnl. Ref. 1



**Use in Pyrotechnics:** As a retardant and to impart a pink color to burning compositions.

**Additional References:**

- 1) "On the Thermogravimetry of Analytical Precipitates," S. Peltier and C. Duval, *Anal. Chim. Acta* 1, 347 (1947)
- 2) E. S. Freeman and B. Carroll, *J. Phys. Chem.* 63, 394 (1958)
- 3) *Nature* 173, 324 (1956)
- 4) "Anhydrous Calcium Oxalate as a Weighing Form for Calcium," C. C. Miller, *Analyst* 78, 186 (1953)
- 5) *C.A.* 47, 5756 (1953)

# CALCIUM OXIDE, CaO

(Lime, Burnt Lime, Fat Lime, Quick Lime, Calx, Calcia)

Specification No.:	—	
Molecular Weight:	56.08	
Crystalline Form:	cubic	1
Color:	colorless	1
Density, g./ml.:	3.346	1
Coefficient of Thermal Expansion, cubical:	$5.0 \times 10^{-7}$	31
Heat of Formation, Kcal./mole at 298°K:	(c)-151.9	9
See Table a		
Free Energy of Formation, Kcal./mole at 298°K:	(c)-144.4	9
See Table a		
a. HEAT AND FREE ENERGY OF FORMATION OF CaO(c)		2

T, °K	H (cal./mole)	F° (cal./mole)
298.16 . . . .	-150,650 ( $\pm 400$ )	-143,250 ( $\pm 500$ )
400 . . . . .	-150,600	-140,600
500 . . . . .	-150,500	-138,250
600 . . . . .	-150,450	-135,800
673 . . . . .	-150,400	-134,000
673 . . . . .	-150,500	-134,000
700 . . . . .	-150,450	-133,350
800 . . . . .	-150,400	-130,900
900 . . . . .	-150,300	-128,500
1000 . . . . .	-150,250	-126,050
1100 . . . . .	-150,200	-123,600
1124 . . . . .	-150,200	-123,050
1124 . . . . .	-152,450	-123,050
1200 . . . . .	-152,350	-121,050
1300 . . . . .	-152,200	-118,450
1400 . . . . .	-152,100	-115,850
1500 . . . . .	-151,950	-113,300
1600 . . . . .	-151,800	-110,700
1700 . . . . .	-151,650	-108,150
1760 . . . . .	-151,550	-106,650
1760 . . . . .	-188,150	-106,650
1800 . . . . .	-188,000	-104,800
1900 . . . . .	-187,550	-100,200
2000 . . . . .	-187,150	-96,550

## Phase Changes of Metal

T.P., 673°K;  $\Delta H = 115$  cal./g.-atom

M.P., 1124°K;  $\Delta H = 2230$  cal./g.-atom

B.P., 1760°K;  $\Delta H = 36,600$  cal./g.-atom

Calcium Oxide, CaO (page 2)

Free Energy Equations:

Reaction	Range of Validity, °K
1) $\text{Ca (s)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{CaO (c)}$ $\Delta F_f^\circ = -151,850 - 6.56T \log T + 1.46 \times 10^{-5}T^2 + 0.68 \times 10^5T^{-1} + 43.93T$	298.16 to 673
2) $\text{Ca (s)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{CaO (c)}$ $\Delta F_f^\circ = -151,730 - 4.14T \log T + 0.41 \times 10^{-5}T^2 + 0.68 \times 10^5T^{-1} + 37.63T$	673 to 1124
3) $\text{Ca (l)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{CaO (c)}$ $\Delta F_f^\circ = -153,480 - 1.36T \log T - 0.29 \times 10^{-5}T^2 + 0.68 \times 10^5T^{-1} + 31.49T$	1124 to 1760
4) $\text{Ca (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{CaO (c)}$ $\Delta F_f^\circ = -194,670 - 718T \log T - 0.29 \times 10^{-5}T^2 + 0.68 \times 10^5T^{-1} + 73.84T$	1760 to 2000
Entropy, cal./deg./mole at 298°K:	(c) 9.5 (gas) 52.3

See Table b

b. HEAT CONTENT AND ENTROPY OF CaO (c)  
(Base, crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	1100	3.17	1300	12,110	17.38
500	2230	5.69	1400	13,430	18.36
600	3400	7.32	1500	14,760	19.28
700	4600	9.67	1600	16,100	20.14
800	5820	11.30	1700	17,440	20.96
900	7040	12.73	1800	18,770	21.72
1000	8270	14.05	1900	20,130	22.45
1100	9520	15.22	2000	21,480	23.15
1200	10,800	16.34			

CaO(c):

Enthalpy:  $H_T - H_{298.15} = 11.67T + 0.54 \times 10^{-5}T^2 + 1.56 \times 10^5T^{-1} - 4051$   
(0.3 percent; 298-2000°K)

Heat Capacity:  $C_p = 11.67 + 1.08 \times 10^{-5}T - 1.56 \times 10^5T^{-2}$

c. HEAT CONTENT AND ENTROPY OF CaO (gas)  
(Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	825	2.38	1000	6005	10.25
500	1665	4.25	1200	7775	11.87
600	2515	5.80	1400	9545	13.23
700	3380	7.13	1600	11,325	14.42
800	4250	8.30	1800	13,115	15.47
900	5125	9.33	2000	14,910	16.42



# Calcium Oxide, CaO (page 3)

Enthalpy:  $H_T - H_{298.15} = 8.70T + 6.08 \times 10^{-5}T^2 + 0.74 \times 10^{-6}T^3 - 2849$   
(0.2 percent; 298° - 2000°K)

Heat Capacity:  $C_p = 8.70 + 0.16 \times 10^{-5}T - 0.74 \times 10^{-8}T^2$

Melting Point: 2843°K (2570°C)

Heat of Fusion, Kcal./mole: 12

Boiling Point: 3123°K (2850°C)

Heat of Vaporization: —

Transition Point: —

Heat of Sublimation: —

Heat Capacity, cal./deg./mole: (solid) 10.23

See also equations under Tables b and c

Decomposition Temperature and Products: —

Dissociation Pressure:  $\log_{10} P_{mm} = 2.74/10^4T + 9.97$  (over the temperature range, 1600 - 1750°K)

See also Refs. 42V7 and 44B2 for additional values

## X-Ray Crystallographic Data:

System	Space Group	a	Molecules/Unit Cell
cubic	$O_h^F$	4.797	4

Hygroscopicity: Very hygroscopic. Combines with water to form  $Ca(OH)_2$ .

Keep containers dry and tightly closed.

Solubility Data: In water, 0.131 at 10°C:

0.0% at 80°C:

reacts to form  $Ca(OH)_2$

In acids, glycerol:

soluble

In alcohol:

insoluble

Health Hazard: Caustic reaction on skin and respiratory system. The dust is an industrial hazard. Causes dermatitis. Treat with large quantities of water.

## Safety Classifications:

OSM: not listed

ICC: not listed

U.N.: corrosive

Fire and Explosion Hazard: Slightly dangerous. Produces heat on contact with water, steam, acids, or acid fumes.

Electrostatic Sensitivity: —

Use in Pyrotechnics: Calcium oxide is a product of high temperature burning of calcium and many of its compounds.

## Additional References:

1) Ref. 64

2) "Vapor Pressure Determination of BaO, SrO and CaO, and Their Mixtures from Measurements of the Rate of Evaporation," A. Claassen and C. Veenemans, Zeit. Physik 80, 342 (1933); cited by Ref. 65

# CALCIUM PERCHLORATE (ANHYDROUS), $\text{Ca}(\text{ClO}_4)_2$

Refs.

Percent Oxygen:	53.56	
Specification No.:	—	
Molecular Weight:	238.99	
Crystalline Form:	cubic	1
Color:	colorless	1
Density, g./ml.:	—	
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	(estd.) -178	72
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	396°K (123°C)	65
Heat of Fusion:	—	
Boiling Point:	decomposes	65
Values in the literature range from less than 573°K (300°C) to about 683°K (410°C)		
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature:	bubbling slight at 258°C, vigorous at 285°C	47
LTA and TGA, see Refs. 33, 47		
Decomposition Products:	$\text{CaCl}_2 + \text{O}_2$ with traces of $\text{CaO}$ and $\text{Cl}_2$	Addnl. Ref. 1
Vapor Pressure:	—	
X-Ray Crystallographic Data for $\text{Ca}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ :		
System	Space Group	a c Molecules/Unit Cell
hexagonal	$\text{C}_{6v}^2$	7.71 5.42 2
		65
Hygroscopicity:	deliquescent	1
Solubility Data: In water:	188.6 g./100 g. at 25°C very soluble in hot water	1
Solubility in Organic Solvents at 25°C:		
Solvent	g./100 g. solvent	
acetone	61.76	
ethyl acetate	113.5	
ethyl alcohol	156.2	
ethyl ether	0.26	
methyl alcohol	237.4	
		65, 72, 77

**Calcium Perchlorate (Anhydrous),  $\text{Ca}(\text{ClO}_4)_2$  (page 2)**

**Health Hazard:**  $\text{CaClO}_4$  is a moderate irritant to the skin and mucous membranes. Avoid contact with skin. A weak muscular poison. It is not cumulative and not reduced in the body. 12, 65

**Safety Classifications:**

**OSM:** Class 1. Class 2 when not packed in original containers or equivalent.

**ICC:** Oxidizing material; yellow label. Listed under "Explosives and Other Dangerous Articles."

**Fire and Explosion Hazard:**  $\text{CaClO}_4$  is a powerful oxidizer. It may cause fires or explosions when shocked or heated or by chemical action with reducing substances such as carbonaceous materials. It forms explosive mixtures with sulphur, powdered magnesium, and aluminum. It also emits highly toxic fumes when heated. 12

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:**  $\text{CaClO}_4$  is used as an oxidizer and to impart a yellow-red color to burning compositions.

**Additional References:**

- 1) C.A. 51, 2439 (1957)

**CALCIUM PHOSPHIDE,  $\text{Ca}_3\text{P}_2$**   
(Photophor)

*Refs.*

**Specification No.:**

**MIL-C-3539**

The specification covers two types: Type A, uncoated, and Type B, coated with  $\text{K}_2\text{Cr}_2\text{O}_7$ . Both types are in the form of solid sticks or lumps  $\frac{1}{4}$  to 1 in. in diameter. The types differ in their rate of reaction with water. When immersed in sea water, Type A shall immediately produce a vigorous reaction with a strong bright flame while Type B is required to give a maximum evolution of smoke and flames at approximately 15 min. after contact with the water. The two types also evolve different amounts of gas for equal masses.

Molecular Weight:	182.20	
Crystalline Form:	cubic	Addnl. Ref. 2
Color:	reddish-brown	Addnl. Ref. 2
Density, g./ml.:	(solid) 2.51 at 15°C	31A
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	(c) -120.5	1, 9
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	about 1873°K (1600°C)	1, 29
Heat of Fusion:	—	
Boiling Point:	—	
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature:	Can be heated to 1250°C without decomposing but reacts with moist air. Reacts in air about 300°C and becomes incandescent.	Addnl. Ref. 1, 54V8
Decomposition Products:	—	
Vapor Pressure:	—	
X-Ray Crystallographic Data:	—	
Hygroscopicity:	Decomposed on contact with water, evolving spontaneously flammable phosphine.	29, Spec.
Solubility Data:	In water: see Hygroscopicity above	
	In acids: soluble	1
	In alcohol, ether, benzene: insoluble	
Health Hazard:	Dangerous, due to reactivity with water which evolves severely toxic phosphine.	12, 93
Safety Classifications:		
OSM:	not listed	
ICC:	Flammable solid; yellow label. Listed under "Explosives and Other Dangerous Materials."	

**Calcium Phosphide,  $\text{Ca}_3\text{P}_2$  (page 2)**

**Fire and Explosion Hazard:** Liable to spontaneous combustion. Dangerous when heated as it emits highly toxic fumes of oxides of phosphorus. May explode when heated by a flame. See Hygroscopicity.

**Caution:** Keep dry and tightly closed (for this reason it is packaged in soldered tins). Under these conditions no gas should be evolved.

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:** As a fuel and to impart a yellow-red color to burning compositions or to produce smoke and flame.

**Additional References:**

- 1) "Phosphorus and Its Compounds," by V. Waser, Interscience Publishers, Inc., New York (1958)
- 2) M. V. Stackelberg and R. Paulus, Zeit. Physik. Chem. 22B, 305 (1933)

15, 12,  
Addnl. Ref. 1

29, Spec.

## CALCIUM RESINATE (Limed Rosin)

**Formula.** approx.  $\text{Ca}(\text{C}_{19}\text{H}_{31}\text{COO})_2$   
 Calcium resinate is a mixture of the calcium salts of resin acids. These include the abietic and pimaric acid types. For a discussion of rosin, resin, and the resin acids see Ref. 50V2.

**Specification No.:** MIL-C-20470  
 The specification covers two types which differ in purity and granulation. Type 1 is fused and Type 2, precipitated.

**Molecular Weight:** 1849.50 12

**Crystalline Form:** Amorphous powder or lumps. Appears to crystallize imperfectly, but definitely with a head-to-head arrangement of the abietate radicals. 1

**Color:** yellow or white Addnl. Ref. 1

**Density:** \_\_\_\_\_

**Coefficient of Thermal Expansion:** \_\_\_\_\_

**Heat of Formation:** \_\_\_\_\_

**Free Energy:** \_\_\_\_\_

**Entropy:** \_\_\_\_\_

**Melting Point:** \_\_\_\_\_

**Heat of Fusion:** \_\_\_\_\_

**Boiling Point:** \_\_\_\_\_

**Transition Point:** \_\_\_\_\_

**Heat of Sublimation:** \_\_\_\_\_

**Heat Content or Enthalpy:** \_\_\_\_\_

**Heat Capacity:** \_\_\_\_\_

**Decomposition Temperature:** \_\_\_\_\_

**Decomposition Products:** \_\_\_\_\_

**Vapor Pressure:** \_\_\_\_\_

**X-Ray Crystallographic Data:** \_\_\_\_\_

**Hygroscopicity:** Specification grade. Gain in mg./g. at room temperature after equilibrium was established in static and vacuum desiccators. 32 (Table 14)

Time	65% R.H.		75% R.H.		86% R.H.		93% R.H.	
	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.
24 hrs.	14.0	8.8	11.5	14.1	25.4	19.0	27.1	23.4
1 week	12.8	12.1	13.9	12.5	23.2	25.6	23.9	27.5
30 days			14.1		27.7		30.9	

**Solubility Data:** soluble in petroleum solvents 50

**Calcium Resinate (page 2)**

Health Hazard:	unknown	12
Safety Classification:		
OSM:	not listed	
ICC:	Flammable solid: yellow label. Listed under "Explosives and Other Dangerous Materials."	
Fire and Explosion Hazard:	Slight; when heated it can react with oxidizing materials.	17
Electrostatic Sensitivity:	---	
Use In Pyrotechnics:	Calcium resinate is used as a retardant fuel, and binding agent. Imparts a yellow-red color to burning compositions. Use also as a waterproofing agent.	
Additional References:		
1)	"A Comparative Study of the X-Ray Diffraction Patterns and Thermal Transitions of Metal Soaps," M. J. Vold and R. D. Vold, J. Am. Oil Chemists' Soc. 26, 520 (1949)	

# CALCIUM SILICIDE, $\text{CaSi}_2$

Refs.

Specification No.: JAN-C-324

The specification covers two grades which differ in purity and granulation. Grade I is used in smoke mixtures, and Grade II in both smoke mixtures and tracer compositions.

Molecular Weight:	96.26	
Crystalline Form:	glassy solid	1
Color:	—	
Density, g./ml.:	(solid) 2.5	1
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	(c) -36	1, 9
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	1493°K (1220°C) 1020°C	9 44, Addnl. Ref. 2

Heat of Fusion:	—
Boiling Point:	—
Transition Point:	—
Heat of Sublimation:	—
Heat Content or Enthalpy:	—
Heat Capacity:	—
Decomposition Temperature:	—
Decomposition Products:	—
Vapor Pressure:	—

## X-Ray Crystallographic Data:

System	Space Group	a	Axial Angle	Molecules/Unit Cell
hexagonal	$D_{3d}^2$	10.4	$21^\circ 30'$	2

1

Note: The structure is characterized by layers of rings with six Si atoms

Addnl. Refs.  
2, 3

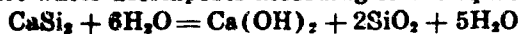
Hygroscopicity: See Solubility (in water)

Solubility Data: In cold water: insoluble

1

In hot water decomposes according to the equation:

Addnl. Ref. 2



In acids and bases: decomposes

Health Hazard: Has caustic action irritating to the skin and respiratory system.

12

May cause dermatitis and irritation to the eyes and mucous membranes.

(Treatment—wash with large volumes of water)

Believed to be nontoxic.

93



**Calcium Silicide,  $\text{CaSi}_2$  (page 2)**

**Safety Classification:**

OSM: not listed  
ICC: flammable solid

**Fire and Explosion Hazard:** Dangerous by chemical reaction with oxidizers. When heated can burn or explode and emit toxic fumes. In contact with water may emit flammable silicon hydrides.

12, Addnl.  
Ref. 1

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:**  $\text{CaSi}_2$  is used as a fuel and to impart a yellow-red color to burning compositions. Used in igniter compositions for tracer projectiles.

17, Addnl.  
Ref. 4

**Additional References:**

- 1) L. Wöhler and L. Schiephake, *Zeit. anorg. Chem.* **151**, 1 (1926)
- 2) "Silicon and Its Binary Systems," A. S. Birezhnoi (Translated from the Russian), Consultants Bureau, New York (1960)
- 3) H. Bohm and O. Hassel, *Zeit. anorg. Chem.* **160**, 152 (1927)
- 4) C.A. **49**, 14326 (1955)

## CALCIUM STEARATE

Formula:	$\text{Ca}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$	Refs.
Specification No.:	JAN-C-263	
Molecular Weight:	607.00	
Crystalline Form:	crystalline powder	
See Addnl. Refs. 2, 3		
Color:	opaque, translucent after heating and cooling	Addnl. Ref. 4
Density:	—	
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 18°C:	$H_f = -662.6$ $H_c = -641.1$	Addnl. Ref. 1
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	452–453°K (179–180°C)	1
Heat of Fusion:	—	
Boiling Point:	decomposes	1
Transition Point: Phase changes at 65, 86, 123, 150, 195 and 350°C. Below 150°C the stable phases are crystalline.		Addnl. Refs. 2, 3
<i>Transition Temperatures and Heats of Transition</i>		
	°C	cal./mole
	89	
	107	9080
	152	
	190	
	58	
	89	
	106	7430
	146	
	187	
Note: Values vary with the source of the samples, which are not pure.		
The 150–195°C phase is a liquid crystal. Quenching from a temperature of 123–150°C produces an unstable crystal, but an unstable vitreous form results on quenching from above 150°C. Technical Ca stearate resembles the pure material but assumes the vitreous form more readily and crystallizes with difficulty.		Addnl. Ref. 2
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature, °C:	above 350	Addnl. Refs. 2, 3, 4
For DTA see Addnl. Ref. 4		

**Calcium Stearate (page 2)**

Decomposition Products: \_\_\_\_\_

Vapor Pressure: \_\_\_\_\_

X-Ray Crystallographic Data:

For X-Ray Diffraction Data see Addnl. Ref. 5

Hygroscopicity: \_\_\_\_\_

Solubility Data: In water:

0.004 g./100 ml. at 15°C  
(not readily wetted)

In alcohol and ether:

insoluble

In methyl alcohol and toluol, g./100 g.:

Temp. °C	methyl alcohol	toluol
25	0.05	0.03
50	0.09	0.47
75		0.22
100		gelled*

\*Ca stearate precipitated on cooling

Health Hazard:

none mentioned

Safety Classifications:

OSM:

not listed

ICC:

not listed

Fire and Explosion Hazard: \_\_\_\_\_

Electrostatic Sensitivity: \_\_\_\_\_

Use in Pyrotechnics: As a fuel and to impart a yellow-red color to burning compositions. Also waterproofing, lubricating, and bonding agent.

**Additional References:**

- 1) L. Médard, *Mém. artillerie franç* 28, 467 (1954)
- 2) "Polymorphic Transformations of Ca Stearate and Ca Stearate Monohydrate," R. Vold et al., *J. Colloid. Sci.* 3, 339 (1948)
- 3) "Crystal Forms of Anhydrous Ca Stearate Derivable from Calcium Stearate Monohydrate," M. Vold et al., *J. Colloid Sci.* 4, 93 (1949)
- 4) "Differential Thermal Analysis of Metal Soaps," G. Hattiangdi et al., *Ind. Eng. Chem.* 41, 2320 (1949)
- 5) "Characterization of Heavy Metal Soaps by X-Ray Diffraction," R. Vold and G. Hattiangdi, *Ind. Eng. Chem.* 41, 2311 (1949)
- 6) "Aero Metallic Stearates," Am. Cyanamid Co., Bound Brook, N. J. (1960)

Addnl. Ref. 6

**CARBON BLACK (DRY) and LAMPBLACK, C**  
**(Cape Cod Black, Gloss Soot, Light Soot, Flame Soot,**  
**Flame Black, Furnace Black, Channel Black, and a wide**  
**variety of proprietary names and numbers)**

Specification No.: Carbon black (dry): MIL-C-11403  
 Lampblack: TT-L-706

Carbon black is an amorphous, quasi-graphitic carbon obtained by burning gas, oils, tars, or other carbonaceous material in an insufficient amount of air to form a deposit of soot. By varying the process and the starting material, properties of the products can be varied considerably. Carbon black is usually one of the following types:

- a) Animal charcoal, made by charring bores, meat, or blood.
- b) Gas black, furnace black, or channel black, made by the incomplete combustion of natural gas.
- c) Lampblack obtained by burning various fats, oils, and resins, under controlled conditions.
- d) Wood and vegetable charcoals.

Carbon blacks are very finely divided. Most individual particles are in the range of 13 to 274 m $\mu$ . As colloids, the particles are negatively charged and show the Brownian movement. Lampblack is amorphous but most carbon blacks are a mixture of the amorphous and crystalline forms. Carbon blacks have an enormous surface per unit mass and are very absorbent. The structure and pH can also be varied over a wide range. Carbon blacks thus find a wide variety of uses.

The individual fine particles are composed of several thousand crystallites. These are in parallel layers of carbon atoms arranged in hexagonal rings as in graphite, but in carbon black the symmetry is much less precise so that the carbon atoms in adjacent layers are rotated about an axis at right angles to their plane. The structure is similar to that of true graphite as the carbon rings are arranged roughly parallel and equidistant but otherwise completely random, and the dimensions within a layer are the same as in graphite. The layer is somewhat larger than in graphite. The effect of heat treatment is to increase the size of the parallel layer groups. On graphitization the material changes discontinuously to the crystalline graphite structure. The usual carbon black is not finely divided graphite. Small angle scattering indicates the existence of clusters of a few hundred angstrom units in size. These clusters are measured by microscope units, by the electron microscope and by surface areas, rather than the much smaller parallel layer groups.

Molecular Weight:	12.011	
Crystalline Form:	fluffy, amorphous powder	1
Color:	black	1
Density, g./ml.:	(solid) 1.8-2.1	1

Refs.

16, 22, 29,  
50V3

Addnl. Refs.  
4, 5, 6, 10, 11

# Carbon Black, C (page 2)

Coefficient of Thermal Expansion, linear :	0.65 $\times 10^{-6}$	Addnl. Ref. 1
see also Ref. 33		
Heat of Formation:	-----	
Free Energy of Formation:	-----	
Entropy:	-----	
Melting Point:	3925-3970°K, sublimes (3652-3687°C)	1
Heat of Fusion:	-----	
Boiling Point:	4473°K (4200 °C)	1
Heat of Vaporization, cal./g.:	11,900	Addnl. Ref. 1
Transition Point:	-----	
Heat of Sublimation, Kcal./mole:	135.7 138 $\pm$ 12	Addnl. Ref. 7 Addnl. Ref. 3
Heat Content or Enthalpy:	-----	
Heat Capacity:	-----	
Decomposition Temperature:	-----	
Decomposition Products:	-----	
Vapor Pressure:	-----	

Press. mm.	04	20	120	240	760	Addnl. Ref. 8	
Temp. °C	2375	2935	3250	3490	3760		
Press. mm.	243	327	380	509	608	760	Addnl. Ref. 9
Temp. °C	4015	4052	4801	4117	4137	4190	

## X-Ray Crystallographic Data:

See Addnl. Refs. 3, 4, 10, 11

## Hygroscopicity:

Solubility Data: In water, acids, and alkalies: insoluble

1

Health Hazard: Considered nontoxic. Prolonged internal use may cause vitamin and mineral deficiency and interfere with digestion.

12, 25, 29

## Safety Classifications:

OSM: Atmospheres containing carbon black are included under hazardous locations, class II.

ICC: not listed

Fire and Explosion Hazard: Slight when exposed to heat or flame. Lampblack made by incomplete combustion of petroleum: may heat spontaneously when freshly bagged. It has great affinity for liquids and heats spontaneously on contact with drying oils. It should be thoroughly cooled before bagging and stored in a cool, dry place away from oxidizing materials. Lampblack dust can be exploded. See data following:

12, 50V6

Carbon Black, C (page 3)

Explosibility of Lampblack:

Concentration	Max. Press.	Avg. Rate of Press. Rise	Max. Rate of Press. Rise
(mg./l.)	(lbs./sq. in.)	(lbs./sq. in./sec.)	(lbs./sq. in./sec.)
100	10	13	119

86

Ignition Temperature, °C:

Carbon black (produced in reducing atmosphere) 535

Thermal carbon blacks: 449-485

Lampblack (oxidizing atmosphere): 352-362

Carbon blacks (natural gas): 313-324

Addnl. Ref. 1

Heat of Combustion (at constant volume), cal./g.:

Carbon amorphous: 8130

Carbon black (dried at 100°C): 7810

(degassed at 1000°C): 8270

Addnl. Ref. 2

Specific Heat at 25°C, g./cal./g. 0.2

Addnl. Ref. 1

Use in Pyrotechnics: Lampblack is used by the Chemical Corps as a pigment in protective coatings.

Additional References:

- 1) "Industrial Carbon," C. L. Mantell, D. Van Nostrand Co., Inc., Princeton, N. J. (1946)
- 2) L. Médard, *Mém. artillerie franç.* 28, 485 (1954)
- 3) "Ionization and Dissociation by Electron Impact, Methylene, Methyl and Methane," A. Langer et al., *J. Chem. Phys.* 22, 1836 (1954)
- 4) *Chem. Eng. News* 23, 2078 (1945)
- 5) "Carbon Black," L. Cohan and H. Cohan, Vol. 5, pt II, "The Science of Petroleum," B. T. Brooks and A. E. Dunstan, Eds., Oxford University Press, New York (1953)
- 6) J. D. Bernal, *Proc. Royal Soc.* 106A, 749 (1924)
- 7) E. Lindholm, *C.A.* 51, 6345 (1957)
- 8) A. Thiel and F. Rister, *Zeit. anorg. Chem.* 132, 125, 153 (1923)
- 9) H. Kohn, *Zeit. Physik* 3, 143 (1920)
- 10) "An X-Ray Study of Carbon Black," J. Biscoe and B. E. Warren, *J. Appl. Phys.* 13, 364 (1942)
- 11) "X-Ray Study of Carbon Black," B. E. Warren, *J. Chem. Phys.* 2, 551 (1934)

**CARBON TETRACHLORIDE, CCl<sub>4</sub>**  
(Tetrachloromethane, Benzoinoform)

Specification No.:	O-C-141	Refs.
Marking: The Air Force requires that each package bear a label as follows: "Caution: Volatile poisonous solvent. Use with adequate ventilation. Avoid prolonged breathing of vapor. Avoid contact with skin."		1, 11
Molecular Weight:	153.84	
Normal Color and Form:	colorless liquid	1
Density, g./ml.:	(liquid) 1.595 at 20/4 1.63195 at 0/4°C	1
Coefficient of Thermal Expansion, cubical, 0-76°C:	$1.236 \times 10^{-4}$	1, 3
$V_t = V_0 + 1.8384t + 0.89881t^2 + 1.35135 \times 10^{-5}t^3$		
Heat of Formation, Kcal./mole at 298°K:	(gas) -25.5 (liquid) -33.3	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(gas) -15.3 (liquid) -16.4	1, 9
Entropy, cal./deg./mole at 298°K:	(gas) 73.95 (liquid) 51.25	1, 9
See table below		
Melting Point:	250.3°K (-22.8°C)	9
Heat of Fusion, Kcal./mole:	0.60	9
Boiling Point:	349.9°K (76.8°C)	9
Heat of Vaporization, Kcal./mole:	7.17	9
Transition Point:	225.5°K (-47.6°C)	9
Heat of Transition, Kcal./mole:	1.09	9
Heat of Sublimation:	—	

**HEAT CONTENT AND ENTROPY OF CCl<sub>4</sub>(g)**  
(Base, ideal gas at 298.15°K)

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	2140	6.16	1000 . . . . .	16,570	27.99
500 . . . . .	4395	11.19	1100 . . . . .	19,080	30.38
600 . . . . .	6740	15.46	1200 . . . . .	21,610	32.58
700 . . . . .	9150	19.17	1300 . . . . .	24,140	34.61
800 . . . . .	11,600	22.45	1400 . . . . .	26,680	36.49
900 . . . . .	14,080	25.37	1500 . . . . .	29,220	38.24

**Carbon Tetrachloride, CCl<sub>4</sub> (page 2)**

CCl<sub>4</sub> (g):

Enthalpy:  $H_T - H_{298.15} = 24.17T + 0.60 \times 10^{-2}T^2 + 4.10 \times 10^{-5}T^3 - 8635$   
(0.3 percent; 298° - 1500°K)

Heat Capacity:  $C_p = 24.17 + 1.20 \times 10^{-2}T - 4.10 \times 10^{-5}T^2$

Heat Capacity, cal./deg./mole:

(liquid) 31.47  
(gas) 19.96

Decomposition Temperature: Noticeable at 150°C particularly in the presence of Cl acceptors, e.g., metals and metal oxides.

Decomposition Products: Phosgene may be formed, especially in the presence of metals.

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	-50.0	-19.6	+4.2	23.0	57.8	76.7	-22.6

X-Ray Crystallographic Data:

Interatomic Distances and Molecular Configuration:

C-Cl, 1.76 Å ± 0.01; Cl-Cl, 2.86 ± .01

Tetrahedral model confirmed spectroscopically

Hygroscopicity:

Solubility Data: Solubility of water in CCl<sub>4</sub> is 0.008% by weight at 20°C. Solubility in water, 0.8 g./100 ml. at 20°C. CCl<sub>4</sub> is miscible in all proportions with alcohol, ether, chloroform, benzene, halogenated hydrocarbons, and most solvents.

Health Hazard: CCl<sub>4</sub> is a systemic poison with a narcotic action resembling that of chloroform. It may cause death through respiratory failure, and can cause serious effects to kidneys, liver, lungs, and the nervous system. It can be fatal when taken internally. Dermatitis may result from repeated skin contact, and its vapors are toxic.

M.A.C.: 25 parts per million in air for an 8-hr. work day.

Caution: Do not use CCl<sub>4</sub> to fight fire in unventilated spaces such as small rooms or closets. Store in airtight drums.

Note: CCl<sub>4</sub> poisoning is detectable in the blood and urine.

Safety Classifications:

OSM: not listed

ICC: not listed

Fire and Explosion Hazard: CCl<sub>4</sub> is not combustible, but its vapor is toxic. It is dangerous when heated to decomposition due to formation of highly toxic phosgene.

Electrostatic Sensitivity:

Azeotrope: CCl<sub>4</sub> forms an azeotrope with water which boils at 66°C at 1 atm. and contains 4.1% water.

4

4, 9

Adm. Refs.  
2, 3, 4

1

85

55

53V1

12, 14, 29

12, 14, 29

53V2



**Carbon Tetrachloride, CCl<sub>4</sub> (page 3)**

Use in Pyrotechnics: CCl<sub>4</sub> is used as a noncombustible solvent and fire retardant in certain compositions.

**Additional References:**

- 1) Ref. 52
- 2) "Poisonous Gases from Carbon Tetrachloride Fire Extinguishers," A. C. Fieldner et al., J. Franklin Inst. 190, 543 (1920)
- 3) "Determination of Phosgene," A. C. Fieldner et al., Ind. Eng. Chem. Anal. Ed. 8, 20 (1936)
- 4) "Mass Spectrographic Study of the Species CS, SO, and CCl<sub>2</sub> Produced in Primary Heterogeneous Reactions," L. P. Blanchard and P. LeGoff, Can. J. Chem. 35, 89 (1957)

## CASTOR OIL

(Ricinus Oil, Oil of Palma Christi, Tangan-Tangan Oil,  
Ricinus Communis)

Refs.

1, 29

**Formula:** Castor oil is a natural product of somewhat variable composition.

**Specification No.:**

MIL-C-15179A  
(dehydrated)

Castor oil is a light yellow to brownish oil obtained from the seed beans of the castor plant. When pure and fresh, it is nearly colorless and transparent. The hot pressed oil is brownish. Castor oil does not readily turn rancid, and is classed as a non-drying oil.

Dehydrated castor oil must be made by the dehydration of castor oil and polymerization of the resulting product, without admixture of other oils.

**Molecular Weight:**

castor oil is a variable  
natural product

**Normal Color and Form:**

pale yellow oil

29

**Density, g./ml.:**

(liquid) 0.960-967

1

**Coefficient of Thermal Expansion:**

---

**Melting Point:**

turbid at 261°K (-12°C),  
solid at 255-258°K  
(-17 to -18°C)

1

**Boiling Point:**

586°K (313°C)

12

**Decomposition Temperature:**

---

**Decomposition Products:**

---

**Vapor Pressure:**

---

**Hygroscopicity:**

---

**Solubility Data:** Miscible with absolute ethyl alcohol, methanol, ether, chloroform, glacial acetic acid.

29

**Health Hazard:**

slight, used medicinally

**Safety Classifications:**

OSM:

not listed

ICC:

not listed

**Fire and Explosion Hazard:**

combustible

**Flash Point, °F:**

445 (closed cup);  
545 (open cup)

75

**Autoignition Temperature, °F:**

905

75

**To fight fire:**

use foam, dry chemical,  
CCl<sub>4</sub>, or water

75

**Electrostatic Sensitivity:**

---

**Use in Pyrotechnics:** Castor oil is used as a fuel, as a waterproofing and binding agent, and to reduce sensitivity to friction.

17

See Addnl. Refs.

**Castor Oil (page 2)**

**Castor oil composition, %:**

diglycerides of ricineleic acid:	80-86
oleic acid:	7-9
linoleic acid:	3-3.5
stearic acid:	0.2
dihydrostearic acid:	0.6-1.8
tocophorol:	about 0.05

16  
29

**Castor oil is dextro rotary and has the following characteristics:**

Refractive index:  $n_D^{20} = 1.473-1.477$   
 $n_D^{25} = 1.466-1.473$

Viscosity at 25°C, poises: 6-8

Surface tension at 20°C, dynes/cm.: 39.0

80°C, dynes/cm.: 35.2

Acid value: 0.12-0.8

Saponification value: 175-183

Iodine value (Wijs): 84

Reichert Meissl number: 1.4

Maumené number: 46-47

Acetyl value: 146-150.5

Unsaponifiable matter: 0.6

Specific heat, cal./g., at 40°C: 0.52

at 200°C: 0.59

1

50V6

**Additional References:**

- 1) "Explosives, Matches, and Fireworks," J. Reilly, The University Press, Cambridge, England (1938)
- 2) "Fats and Oils," H. G. Kirschenbauer, Reinhold Publishing Corp., New York (1944)

# CHROMIC ACID, CrO<sub>3</sub>

(Chromic Trioxide, Chromic Anhydride,  
Chromium (VI) Oxide, Red Oxide of Chromium)

Percent Oxygen:	48.00
Specification No.:	(for technical grade) O-C-3038
Molecular Weight:	100.01
Crystalline Form:	rhombic
Color: red (color darkens with rise in temperature and is restored on cooling)	
Density, g./ml.:	(solid) 2.70
Coefficient of Thermal Expansion:	—
Heat of Formation, Kcal./mole at 298°K:	-142.1 ± 1 -138.5 ± 2.5

Addnl. Ref. 8 gives literature values from -140 to -147

Free Energy of Formation at 298°K:	-120.2
------------------------------------	--------

## HEAT AND FREE ENERGY OF FORMATION, CrO<sub>3</sub>(c)

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16 . . . .	-140,000 (± 3000)	-121,000 (± 3500)
400 . . . . .	-139,000	-114,500
471 . . . . .	-139,000	-110,000
471 . . . . .	-135,000	-110,000
500 . . . . .	-134,500	-108,500
600 . . . . .	-133,000	-108,500

Entropy, cal./deg./mole at 298°K:	(solid) 17.5 17.2 ± 2.5
-----------------------------------	----------------------------

## Free Energy Equations:

Reaction	Range of Validity, °K
1) Cr (c) + ½ O <sub>2</sub> (g) = CrO <sub>3</sub> (c) Δ F <sub>T</sub> <sup>o</sup> = -141,590 - 13.82T log T + 103.90T	298.16 to 471
2) Cr (c) + ½ O <sub>2</sub> (g) = CrO <sub>3</sub> (l) Δ F <sub>T</sub> <sup>o</sup> = -141,580 - 32.24T log T + 153.14T	471 to 600

Melting Point, °C:	196 (with decomposition) 197	1A, 31 Addnl. Ref. 8
Heat of Fusion, Kcal./mole	3.77	2
Boiling Point, °K:	decomposes	1A
Heat of Vaporization:	—	
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	

Refs.  
Addnl. Ref. 8

1A  
1A, 54V2  
1A

Addnl. Ref. 7  
24A

6

2

6  
24A

2

**Chromic Acid, CrO<sub>3</sub> (page 2)**

**Decomposition Temperature:**

above 230°C

25

For TGA see Addnl. Ref. 9

For DTA and TGA see Refs. 33 and 54V2

**Decomposition Products**

Cr<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>5</sub>, CrO<sub>2</sub>,  
Cr<sub>2</sub>O<sub>3</sub> + O<sub>2</sub>

54V2  
Addnl. Refs.  
4, 6

**Vapor Pressure:**

—

**X-Ray Crystallographic Data:**

System	Space Group	a	b	c	Molecules/ Unit Cell
orthorhombic	D <sub>2h</sub> <sup>16</sup>	5.70 ± 0.05	8.46 ± 0.03	4.77 ± 0.08	4

Addnl. Ref. 5  
96

**Hygroscopicity:**

deliquesces above 35%  
R.H.

Addnl. Ref. 8

**Solubility Data:**

In water:

166 g./100 ml. at 15°C and  
206.7 at 100°C

1A

In ether, alcohol, H<sub>2</sub>SO<sub>4</sub>:

soluble

**Health Hazard:** Extremely toxic. Local irritant and systemic poison. L.D. (subcutaneously in dogs) 330 mg./kg. Concentrated solutions may cause dermatitic and local ulceration. Inhalation causes irritation to nasal mucosa and respiratory tract. Ingestion may cause nausea, vomiting, diarrhea, renal damage, and death.

29, 12

Caution—not for internal use.

**Safety Classifications:**

OSM:

not specifically mentioned

ICC:

oxidizing material, yellow  
label

M.C.A.:

warning label required

**Fire and Explosion Hazard:** Dangerous; may oxidize organic compounds with explosive violence. Contact with combustible material may cause fire and evolution of highly toxic fumes.

12, 29

Foamite is ineffective against a chromic acid fire as the acid supplies its own oxygen. Carbon tetrachloride should not be used on a chromic acid fire. Water is the only effective agent.

Addnl. Ref. 8

**Use in Pyrotechnics:**

as an oxidizer

**Additional References:**

- 1) "Preparation of Ferromagnetic Chromium Dioxide," B. Kubota, J. Phys. Soc. Japan 15, 1706 (1960)  
(See note below)
- 2) "Decomposition of Higher Oxides of Chromium under Various Pressures of Oxygen," B. Kubota, J. Am. Ceram. Soc. 44, 239 (1961)

**Chromic Acid, CrO<sub>3</sub> (page 3)**

Note: Both references above discuss the thermal decomposition of CrO<sub>3</sub> under high oxygen pressure resulting from the oxygen liberated from CrO<sub>3</sub> itself.

- 3) "Chromic Acid in the Metal Finishing Industry," Diamond Alkali Co., Cleveland, Ohio (1953)
- 4) "The Products of Thermal Decomposition of Chromium Trioxide," R. S. Schwartz et al., J. Am. Chem. Soc. 74, 1676 (1952)
- 5) "The Crystal Structure of Chromium Trioxide," A. Bystrom and K. A. Wilhelmi, Acta. Chem. Scand. 4, 1131 (1950). C.A. 45, 3679 (1951)
- 6) C.A. 45, 21319 (1959)
- 7) "The Heat of Formation of Ammonium Dichromate," C. A. Neugebauer and J. L. Margrave, J. Phys. Chem. 61, 1429 (1957)
- 8) "Chromium," M. Judy, Reinhold Publishing Corp., New York (1956)
- 9) C.A. 42, 422 (1948)

# CHROMIC OXIDE, Cr<sub>2</sub>O<sub>3</sub>

(Chromium (III) Oxide, Chromium Sesquioxide, Chrome Green, Green Cinnabar, Green Oxide of Chromium, Anadonis Green, Ultramarine Green, Chrome Ochre, Oil Green, Leaf Green, Green Rouge)

Percent Oxygen: 31.57  
 Specification No.: not listed  
 Molecular Weight: 152.02  
 Crystalline Form: hexagonal  
 Color: green

Commercial materials vary from a brownish green, to greyish green, to olive green to bright grass green.

Density g./ml.: (solid) 5.21

Coefficient of Thermal Expansion:

T, °C	% Linear Expansion bet. 100°C and Indicated Temp.	10° X Mean Thermal Coeff. of Expansion bet. 100°C and Indicated Temp.
200 . . . . .	0.07	6.8
400 . . . . .	0.14	7.1
600 . . . . .	0.36	7.1
800 . . . . .	0.51	7.3
1000 . . . . .	0.66	7.3
1200 . . . . .	0.82	7.4

Heat of Formation, Kcal./mole at 298°K: -269.7  
 -272.7 ± 4  
 -272.65  
 -268.5

## a. HEAT AND FREE ENERGY OF FORMATION OF Cr<sub>2</sub>O<sub>3</sub> (α, β)

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16 . . . .	-272,650 (± 350)	-253,150 (± 500)
298.16 . . . .	-272,550	-253,150
400 . . . . .	-272,250	-246,550
500 . . . . .	-271,850	-240,200
600 . . . . .	-271,500	-233,900
700 . . . . .	-271,200	-227,650
800 . . . . .	-270,850	-221,450
900 . . . . .	-270,650	-215,250
1000 . . . . .	-270,450	-209,150
1100 . . . . .	-270,300	-203,000
1200 . . . . .	-270,150	-196,900
1300 . . . . .	-270,100	-190,800
1400 . . . . .	-270,100	-184,700

Refs.

Addnl. Ref. 5

1A

1A

54V2

1A

Addnl. Ref. 5

9, 31A

Addnl. Ref. 4

2

Addnl. Ref. 3

Chromic Oxide, Cr<sub>2</sub>O<sub>3</sub> (page 2)

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
1500 . . . . .	-270,150	-178,600
1600 . . . . .	-270,200	-172,450
1700 . . . . .	-270,300	-166,400
1800 . . . . .	-270,500	-160,250
1823 . . . . .	-270,550	-158,850
1823 . . . . .	-278,950	-158,850
1900 . . . . .	-279,000	-153,800
2000 . . . . .	-279,100	-147,200

Free Energy of Formation, Kcal./mole at 298°K: -250.3 ± 0.5

Entropy, cal./deg./mole at 298°K: 19.4

Addnl. Ref. 4  
1A, 9, 31A

b. HEAT CONTENT AND ENTROPY Cr<sub>2</sub>O<sub>3</sub> (c)  
(Base, α-crystals at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
298.16 (β) . .	100	0.34	1200 . . . . .	26,430	40.11
400 . . . . .	2740	7.94	1300 . . . . .	29,550	42.60
500 . . . . .	5540	14.19	1400 . . . . .	32,670	44.91
600 . . . . .	8380	19.36	1500 . . . . .	35,790	47.07
700 . . . . .	11,280	23.82	1600 . . . . .	38,920	49.08
800 . . . . .	14,230	27.76	1700 . . . . .	42,050	50.98
900 . . . . .	17,210	31.27	1800 . . . . .	45,180	52.77
1000 . . . . .	20,240	34.46	1900 . . . . .	48,320	54.47
1100 . . . . .	23,320	37.40	2000 . . . . .	51,460	56.08

Cr<sub>2</sub>O<sub>3</sub> (β):

H<sub>T</sub> - H<sub>298.15</sub> = 28.53T + 1.10 × 10<sup>-5</sup>T<sup>2</sup> + 3.74 × 10<sup>5</sup>T<sup>-1</sup> - 9758  
(0.2 percent; 298° - 1800°K)

C<sub>p</sub> = 28.53 + 2.20 × 10<sup>-5</sup>T - 3.74 × 10<sup>5</sup>T<sup>-2</sup>

Free Energy Equations:

- | Reaction   | Range of Validity, °K |
|--|-----------------------|
| 1) 2 Cr (c) + ½ O <sub>2</sub> (g) = Cr <sub>2</sub> O <sub>3</sub> (β)  | 298.16 to 1823        |
| Δ F <sub>T</sub> <sup>o</sup> = -274,670 - 14.07T log T + 2.01 × 10 <sup>5</sup> T <sup>2</sup> + 0.69 × 10 <sup>5</sup> T <sup>-1</sup> + 105.61T |                       |
| 2) 2 Cr (l) + ½ O <sub>2</sub> (g) = Cr <sub>2</sub> O <sub>3</sub> (β)  | 1823 to 2000          |
| Δ F <sub>T</sub> <sup>o</sup> = -278,030 + 2.33T log T - 0.35 × 10 <sup>5</sup> T <sup>-2</sup> + 1.57 × 10 <sup>5</sup> T <sup>-1</sup> + 58.29T  |                       |

Melting Point, °C: The range of values listed in the literature vary as much as 500°C.

Lowest value	1900
Highest value	2435

2

31A  
Addnl. Ref. 5



**Chromic Oxide, Cr<sub>2</sub>O<sub>3</sub> (page 3)**

Heat of Fusion, Kcal./mole:	25	6
Boiling Point, °K:	decomposes at 3300 ± 300	8
Transition Point, °K: C <sub>II</sub> to C <sub>I</sub>	306	9, 41
	298	2
Heat of Transition, Kcal./mole:	0.1	2
Heat of Sublimation:	—	
Heat Content or Enthalpy:		
See Table b		
Heat Capacity:		
See Table b		
Decomposition Temperature:	3300 ± 300	8
See also Addnl. Ref. 1		
For DTA see 54V11		
Decomposition Products:	—	
Dissociation Pressure:		

Oxygen Pressures over Cr<sub>2</sub>O<sub>3</sub>

Addnl. Ref. 5

Press. atm.	$7.4 \times 10^{-25}$	$5.1 \times 10^{-23}$	$3.8 \times 10^{-22}$
Temp. °C	895	968	1002

For Dissociation Pressure curve see Ref. 54V11

**X-Ray-Crystallographic Data:**

System	Space Group	a	c	Molecules/Unit Cell
Hexagonal	D <sub>3d</sub> <sup>6</sup>	4.954	13.548 at 26°C	6

97V5

**Hygroscopicity:**

Solubility Data: In water: insoluble

In acids, alkalies, or alcohol: slightly soluble

Health Hazard: Poisonous. Corrosive on skin and mucous membranes.

**Safety Classifications:**

OSM: not listed

ICC: not listed

**Fire and Explosion Hazard:**

**Electrostatic Sensitivity:**

Use in Pyrotechnics: Product of the burning of chromium and some chromium compounds.

**Additional References:**

- 1) "Decomposition of Higher Oxides of Chromium under Various Pressures of Oxygen," B. Kubota, J. Amer. Ceram. Soc. 44, 239 (1961)
- 2) "The Volatilization of Chromium Oxide," D. Caplan and M. Cohen, J. Electrochem. Soc. 108, 438 (1961)

**Chromic Oxide,  $\text{Cr}_2\text{O}_3$  (page 4)**

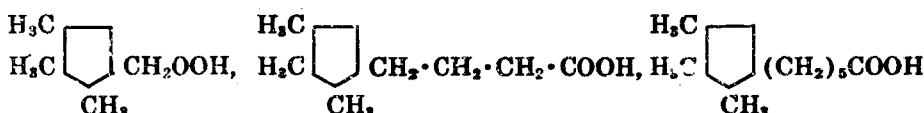
- 3) "Thermodynamics of the Oxidation of Chromium," J. N. Ramsey et al., *J. Electrochem. Soc.* 103, 135 (1956)
- 4) "Heats of formation of chromium oxide and cadmium oxide from combustion calorimetry," A. D. Mah, *J. Am. Chem. Soc.* 76, 3363 (1954)
- 5) "Chromium," M. Judy, Reinhold Publishing Corp., New York (1956)

## COBALT NAPHTHENATE

Cobalt naphthenate is a solution of the cobalt salts of mixed naphthenic acids in mineral spirits. The product contains about 6% cobalt and is standardized on this basis. Chemical and physical properties of cobalt naphthenate cannot be described in the usual manner because the naphthenic acid usually represents a mixture of various cyclopentane monocarboxylic acids, containing on the average about 12 carbon atoms. The carboxyl group is usually separated from the cyclopentane group by at least one methylene group, but sometimes there may be more than one. The balance of the carbons is made up by alkyl substitution on the cyclopentane nucleus. The acids vary considerably depending on the particular source of the petroleum crude from which they are derived. The cobalt is primarily in the cobaltous form.

Chemically the naphthenic acids have been classified as carboxylic acids of the general formulas  $C_nH_{2n-2}COOH$  and  $C_nH_{2n-4}COOH$ , with most of them in the first group. They are derivatives of the 2,3,4-trimethylcyclopentane alkane acids, e.g.

Structural Formula:



Commercially available naphthenic acids are identified by origin and acid number. The lack of a more definite classification is due to the complexity of the mixed acids now known as naphthenic acids and to the absence of information correlating the properties of the acids from different sources.

The general formula has been given as approximately  $Co(RCOO)_2$ , where R is largely a mixture of trimethylcyclopentane alkane radicals.

Specification No.:

TT-D-643

Specification Requirements:

Metal (cobalt), %:	(min.) 5.7 (max.) 6.3
Non-volatile, %:	(max.) 70
Sp. Gr.:	(min.) 0.950 (max.) 1.050
Flash Pt. (closed cup), °F:	(min.) 100

The volatile matter shall be mineral spirits.

Color:	red-blue to purple	50V5
Density, g./ml.:	0.947 to 0.965	50V5
Melting Point:	398°K (125°C)	50V5
Solubility:	soluble in benzene	50V5
Health Hazard:	In the stomach, cobalt naphthenate hydrolyzes to $CoCl_2$ . Although this compound has been used medicinally in cases of iron deficiency (anemia), in doses larger than 100 mg. $CoCl_2$ is toxic.	29V5

Refs.

Addnl. Ref. 1

Addnl. Ref. 2

Addnl. Refs.  
2, 3

50V5

## Cobalt Naphthenate (page 2)

### Safety Classification:

OSM: not listed  
ICC: not listed

Fire and Explosion Hazard: —

Electrostatic Sensitivity: —

Nuodex Products Co. specifications for Cobalt Naphthenate (DMR Cobalt 6%) : Addnl. Ref. 1

Metal content, % :	6.0 ± 0.1
Color (Gardner), max.:	violet blue
Sp. Gr.:	0.935 - 0.980
lbs./gal. (at 80°F) :	7.75 - 3.15
Solids, % max.:	57
80°F Viscosity (max.), Gardner:	A, 0.50 poises
20°F Viscosity (max.), Gardner:	K, 2.75 poises
Flash Pt. (Pensky-Marten closed cup), °F:	104

Use in F. mechanics: As a paint drier. As a catalyst with Laminac 4116 and Lupersol DDM (q.v.).

### Additional References:

- 1) Private communication from W. J. Stewart, Nuodex Products Co., Elizabeth, N. J.
- 2) "Naphthenic Acids and Derivatives," E. R. Littmann and J. R. Klotz, Chem. Revs. 30, 97 (1942)
- 3) "A Manual of Organic Chemistry," G. M. Dyson, Longmans, Green and Co., New York (1950)

# COPPER, Cu

Refs.

Specification No.:	JAN-C-768	
Molecular Weight:	63.54	
Crystalline Form:	cubic	1
Color:	reddish metal	1
Density, g./ml.:	(solid) 8.93-8.95	1
Coefficient of Thermal Expansion:		
	Temp. Range, °C	Coefficient
linear	-191 to + 16	$14.09 \times 10^{-6}$
(electrolytic) linear	25 to 100	$16.8 \times 10^{-6}$
	25 to 300	$17.8 \times 10^{-6}$
	0 to 600	$16.07 \times 10^{-6}$
Equation for Linear Expansion: $l_t = l_0 (1 + .1596 t + 0.102t^2)$		1
where $l_t$ and $l_0$ are the lengths at the temperature $t^\circ\text{C}$ and $0^\circ\text{C}$		
Heat of Formation, Kcal./mole at 298°K:	(gas) 81.1	5
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 71.628	5
Entropy, cal./deg./mole at 298°K:	7.97	5
See Tables a, b, and c		
Melting Point:	1356°K (1083°C)	5
Heat of Fusion, cal./mole:	3120	4, 5
Boiling Point:	2855°K (2582°C)	5
Heat of Vaporization, cal./mole:	72,800	5
Transition Point:	—	
Heat of Sublimation, cal./mole at 298°K:	81,000	5
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 1201	5
	(gas) 2116	9

See Tables a, b, and c

## a. HEAT CONTENT AND ENTROPY OF Cu(c, l) (Base, crystals at 298.15°K; atomic wt. 63.54)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	600	1.73	1100 . . . . .	5190	8.28
500 . . . . .	1215	3.10	1200 . . . . .	5895	8.90
600 . . . . .	1845	4.25	1300 . . . . .	6615	9.47
700 . . . . .	2480	5.23	1357(c) . . . .	7040	9.79
800 . . . . .	3130	6.10	1357(l) . . . .	10,160	12.09
900 . . . . .	3800	6.89	1400 . . . . .	10,480	12.32
1000 . . . . .	4490	7.61	1500 . . . . .	11,230	12.84

**Copper, Cu (page 2)**

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg.	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$
1600 . . . . .	11,980	13.33	2200 . . . . .	16,480	15.71
1700 . . . . .	12,730	13.78	2400 . . . . .	17,980	16.37
1800 . . . . .	13,480	14.21	2600 . . . . .	19,480	16.97
1900 . . . . .	14,230	14.62	2800 . . . . .	20,980	17.52
2000 . . . . .	14,980	15.00			

**Cu(c) :**

Enthalpy:  $H_T - H_{298.15} = 5.41T + 0.75 \times 10^{-5}T^2 - 1680$  (0.3 percent; 298° - 1357°K)

Heat Capacity:  $C_p = 5.41 + 1.50 \times 10^{-5}T$

**Cu(l) :**

Enthalpy:  $H_T - H_{298.15} = 7.50T - 20$  (0.1 percent; 298° - 2800°K)

Heat Capacity:  $C_p = 7.50$

**b. HEAT CONTENT AND ENTROPY OF Cu(g)**

(Base, ideal gas at 298.15°K; atomic wt., 63.54)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	505	1.46	1900 . . . . .	7985	9.22
500 . . . . .	1005	2.57	2000 . . . . .	8495	9.48
600 . . . . .	1500	3.48	2200 . . . . .	9530	9.27
700 . . . . .	1995	4.24	2400 . . . . .	10,590	10.43
800 . . . . .	2495	4.90	2600 . . . . .	11,680	10.87
900 . . . . .	2990	5.49	2800 . . . . .	12,815	11.29
1000 . . . . .	3490	6.01	3000 . . . . .	13,995	11.70
1100 . . . . .	3985	6.49	3500 . . . . .	17,155	12.67
1200 . . . . .	4480	6.92	4000 . . . . .	20,600	13.59
1300 . . . . .	4980	7.32	4500 . . . . .	24,290	14.46
1400 . . . . .	5475	7.69	5000 . . . . .	28,150	15.27
1500 . . . . .	5975	8.03	6000 . . . . .	36,160	16.73
1600 . . . . .	6475	8.35	7000 . . . . .	44,450	18.01
1700 . . . . .	6975	8.66	8000 . . . . .	53,175	19.17
1800 . . . . .	7480	8.94			

**Cu(g) :**

Enthalpy:  $H_T - H_{298.15} = 4.97T - 1482$  (0.1 percent; 298° - 2000°K)

Heat Capacity:  $C_p = 4.97$

Enthalpy:  $H_T - H_{298.15} = 2.86T + 0.53 \times 10^{-5}T^2 + 655$  (0.2 percent; 2000° - 5000°K)

Heat Capacity:  $C_p = 2.86 + 1.06 \times 10^{-5}T$

## Copper, Cu (page 3)

## c. HEAT CAPACITY OF COPPER

Solid from 298 to 1356°K	
Liquid from 1356 to 2855°K	
Gas from 2855 to 3000°K	
t, °K	C <sub>p</sub> (cal./deg./mole)
298	5.85
400	6.01
600	6.31
800	6.61
1000	6.91
1300	7.36
1400 to 2800	7.50
2900	5.89
3000	6.01

Decomposition Temperature: —

Decomposition Products: —

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	B.P.
Temp. °C	1628	1879	2067	2207	2465	2595	1083

X-Ray Crystallographic Data:

System	Space Group	a	Atoms/Unit Cell
cubic	O <sub>h</sub> <sup>1</sup>	3.608	4

Hygroscopicity: (Reduced Cu) cumulative increase in weight after

storage over water for 29 days: 1.9%

storage over H<sub>2</sub>SO<sub>4</sub> for 29 days: 1.0%

2 days in oven at 105°C: 0.9%

In moist air gradually forms green basic copper carbonate, CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>

Solubility Data: In water:

insoluble

In HNO<sub>3</sub>, hot H<sub>2</sub>SO<sub>4</sub>:

soluble

In HCl, NH<sub>4</sub>OH, acetic acid:

very slightly soluble

Health Hazard: Copper is not considered an industrial poison. It is moderately toxic when inhaled or ingested.

Safety Classification:

OSM:

class 2

Fire and Explosion Hazard: The powdered metal is a dangerous fire hazard when exposed to flame or hot sparks. By chemical reaction with oxidizers it may explode. It burns with intense heat. Precautions should be taken to prevent water from contacting the material. Store and process only in buildings adequately vented to prevent accumulation of evolved hydrogen

**Copper, Cu (page 4)**

which results from the reactions of powdered metal and moisture. In the repair or maintenance of buildings use only non-sparking tools after the metal powder or dust has been removed. In fighting fire use no water; use powdered graphite, dolomite, or sodium chloride.

Electrostatic Sensitivity:	not ignited by electric spark	49
Ignition Temperature: (Reduced Cu)		
Dust Cloud, °C:	700	49
Quiescent Powder:	oxidized rapidly at 270°C with no ignition	51
Use in Pyrotechnics: Copper is used as a fuel. It produces a blue-green color in burning compositions.		20, 50

**Additional Reference:**

- 1) Ref. 64



**CUPROUS OXIDE, Cu<sub>2</sub>O**  
(Cuprite)

Specification No.:	MIL-C-15169
The spec. covers two types, Type I and Type II, which differ in purity.	
Molecular Weight:	148.08
Crystalline Form:	octagonal, cubic
Color:	yellow, orange, red, or dark brown, according to the method of preparation
Density, g./ml.:	(solid) 6.0
Coefficient of Thermal Expansion, cubic at 40°C:	$2.79 \times 10^{-6}$
linear at 40°C:	$9.3 \times 10^{-7}$
Heat of Formation, Kcal./mole at 298°K:	-39.84
See Table a	
Free Energy of Formation, cal./mole at 298°K:	-34.98
See Table a	

Refs.

1

79

1

54V3

1, 9

1, 8

a. HEAT AND FREE ENERGY OF FORMATION OF Cu<sub>2</sub>O (c, l)

T, °K	H (cal./mole)	F° (cal./mole)
298.16 . . . .	-40,400 (± 1550)	-35,000 (± 1500)
400 . . . . .	-46,200	-33,200
500 . . . . .	-40,100	-31,500
600 . . . . .	-39,900	-29,800
700 . . . . .	-39,700	-28,200
800 . . . . .	-39,500	-26,500
900 . . . . .	-39,300	-24,900
1000 . . . . .	-39,000	-23,300
1100 . . . . .	-38,800	-21,800
1200 . . . . .	-38,400	-20,200
1300 . . . . .	-38,000	-18,700
1357 . . . . .	-37,700	-17,900
1357 . . . . .	-43,900	-17,900
1400 . . . . .	-43,700	-17,100
1500 . . . . .	-43,100	-15,200
1502 . . . . .	-43,100	-15,200
1502 . . . . .	-29,700	-15,200
1600 . . . . .	-29,200	-14,200
1700 . . . . .	-28,000	-13,300
1800 . . . . .	-28,300	-12,400
1900 . . . . .	-27,800	-11,600
2000 . . . . .	-27,400	-10,700

Phase Changes of Metal

M.P., 1357°K

Δ H = 3120 cal./g.-atom

**Cuprous Oxide, Cu<sub>2</sub>O (page 2)**

Entropy, cal./deg./mole at 298°K:	24.1 22.44	3, 4, 9 2
Melting Point:	1502°K (1229°C)	2, 9
Heat of Fusion, Kcal./mole	13.4	2, 7, 9
Boiling Point:	loses oxygen at 2073°K (1800°C)	1
Transition Point:	—	
Heat of Sublimation:	—	

**b. HEAT CONTENT AND ENTROPY OF Cu<sub>2</sub>O(c)  
(Base, crystals at 298.15°K)**

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	1720	4.96	900 . . . . .	11,000	19.98
500 . . . . .	3470	8.87	1000 . . . . .	13,920	22.10
600 . . . . .	5280	12.26	1100 . . . . .	15,120	24.10
700 . . . . .	7150	15.14	1200 . . . . .	17,320	26.02
800 . . . . .	9050	17.68			

**Cu<sub>2</sub>O(c) :**

Enthalpy:  $H_T - H_{298.15} = 14.90T + 2.85 \times 10^{-5}T^2 - 4696$   
(0.2 percent; 298° - 1200°K)

Heat Capacity:  $C_p = 14.90 + 5.70 \times 10^{-5}T$

Heat Capacity, cal./deg./mole at 298°K: (solid) 16.7

Decomposition Temperature: When heated in air starts to oxidize slowly at about 145°C, and rapidly towards 285°C.

Heated in air it does not dissociate but oxidizes.

Decomposition Products:

Ref 54V3 states that at high temperature Cu<sub>2</sub>O dissociates into copper and oxygen.

Dissociation Pressure:

Press. mm.	.0,65	.0,16	.0,28	.038	.138	.446	8.312	40.19
Temp. °C	500	1000	1500	1800	1900	2000	2300	2500

X-Ray Crystallographic Data:

System	Space Group	a	Molecules/Unit Cell
cubic	O <sub>h</sub>	4.26	2

Hygroscopicity: Cuprous oxide is stable in dry air, but gradually oxidizes to cupric oxide, CuO, in moist air.

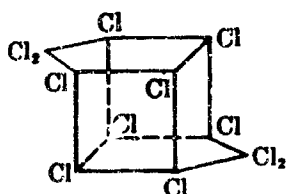
**Cuprous Oxide, Cu<sub>2</sub>O (page 3)**

Solubility Data: In water and alcohol:	insoluble	1
In HCl, NH <sub>4</sub> Cl, NH <sub>4</sub> OH:	soluble	
In HNO <sub>3</sub> :	slightly soluble	
Health Hazard:	slight	12
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard:	—	
Electrostatic Sensitivity:	—	
Use in Pyrotechnics: Cuprous oxide is used as a fuel, and with chlorinated organic compounds as a color intensifier.		17
Additional References:		
1) E. Heyn, Zeit. anorg. Chem. 39, 1 (1904)		

**"DECHLORANE,"  $C_{10}Cl_{12}$**   
**(Dimer of Hexachlorocyclopentadiene)**

Note: The name "Dechlorane" is trademarked by the Hooker Chemical Corp.

Formula:



Specification No.:	not listed
Molecular Weight:	545.6
% Chlorine:	78.3
Crystalline Form:	granular solid
Color:	white
Density:	$2.020 \pm 0.005$ g./cc. at $24.3^\circ\text{C}$
Coefficient of Thermal Expansion:	---
Heat of Formation:	---
Free Energy of Formation:	---
Entropy:	---
Melting Point, $^\circ\text{C}$ :	(sealed tube method) 485
In a DTA run liquifaction started at about $160^\circ\text{C}$	
Heat of Fusion:	---
Boiling Point, $^\circ\text{C}$ :	starts to sublime about 240
Transition Point:	---
Heat of Sublimation:	---
Heat Content or Enthalpy:	---
Heat Capacity:	---
Decomposition Temperature:	
White fumes noted bet. $300^\circ$ – $500^\circ\text{C}$ . These fumes darkened as the temp. was raised. Some decomposition above $500^\circ\text{C}$ .	
For DTA see Ref. 33	
Decomposition Products:	---

Refs.

Addnl. Ref. 3

Addnl. Refs.  
1, 2, 4

Addnl. Ref. 1

Addnl. Ref. 1

Addnl. Refs.  
1, 2, 33

Addnl. Ref. 1

33

Dechlorane,  $C_{10}Cl_{12}$  (page 2)

Vapor Pressure:

Press. mm.	$3 \times 10^{-7}$	$6 \times 10^{-6}$	$3 \times 10^{-1}$
Temp. °C	25	50	197

Addnl. Ref. 1

X-Ray Crystallographic Data:

Hygroscopicity:

Solubility Data: In benzene:

soluble

Addnl. Ref. 3

<i>Solvent</i>	<i>g./100 g. solvent at R.T.</i>
toluene	13.3
xylene	32.7
perchloroethylene	10.3
styrene	17.2
mineral spirits (Stoddard solvent)	5.8

Addnl. Ref. 1

Reactivity: Dechlorane is inert to strong oxidizing and reducing agents such as  $H_2SO_4$ ,  $HNO_3$ , aq.  $NaOH$ ,  $LiAl$ ,  $H_2$ ,  $ClSO_3H$ ,  $H_2$  and  $O_2$  under normal reaction conditions. Unaffected by Zn dust plus  $HCl$ , acetic acid or methanol, also by oxidizing agents such as  $KMnO_4$ ,  $CrO_3$  and  $SO_3$ .

Addnl. Ref. 1

Addnl. Ref. 2

Health Hazard: Only slightly toxic. Essentially not irritating to the skin. Oral L.D. 50 (value determined on rats) approx. 6000 mg./kg.

Addnl. Ref. 1

Safety Classifications:

OSM:	not listed
ICC:	not listed

Fire and Explosion Hazard:

Electrostatic Sensitivity:

Use in Pyrotechnics:

as a color intensifier

Additional References:

- 1) Data obtained from literature prepared by the Hooker Chemical Corp., Niagara Falls, N. Y.
- 2) "An Investigation of the Chlorocarbon,  $C_{10}Cl_{12}$ , M.P.  $485^\circ$  and the Ketone,  $C_{10}Cl_{10}O$ , M.P.  $349^\circ$ ," E. T. McBee et al., J. Am. Chem. Soc. 78, 1511 (1956)
- 3) "The Chemical Behavior of Hexachlorocyclopentadiene. II. Condensation with Trichloroethylene," J. S. Newcomer and E. T. McBee, J. Am. Chem. Soc. 71, 952 (1949)
- 4) "The Structure of the Compound  $C_{10}Cl_{12}$ ," D. H. Zijp and H. Gerding, Rec. trav. chim. 77, 682 (1958)

## DEXTRIN

(Starch Gum, British Gum, Amylin, Gommalin, Vegetable Gum)

Dextrin or dextrines are obtained by treating starch in any one of a number of ways. These include controlled dilute acid hydrolysis of wet starch, the use of certain enzymes, and dry heat. The resultant products, whose properties vary with the source of the starch and the details of the treatment, are represented by the general chemical formula  $(C_6H_{10}O_5)_n \cdot H_2O$ . The  $n$  is, however, much smaller than in the original starch. The various dextrinization treatments of starch lead to complex mixtures resulting from three main types of reaction:

- 1) Hydrolytic cleavage, which yields smaller and more water soluble compounds.
- 2) Transglucosidation, in which a 1-4 glucosidic bond between two  $C_6H_{10}O_5$  units is broken and a 1-6 bond formed with a different  $C_6H_{10}O_5$  unit, with the formation of a branch point. This reaction produces branched molecules and little change in molecular weight.
- 3) Some repolymerization and condensation of smaller molecules.

Because the polymolecularity of the original starches differ and various treatments result in a mixture of the three main reactions, the products differ in size, distribution of molecules, and in extent of branching, and thus have different properties.

Dextrins are distinguished from starch by the violet and red colors that dextrins give with iodine solution

Dextrins are usually characterized by giving the source or kind of starch used, the color of the dry products, their solubility in water, and the viscosity of their water dispersions. The following table gives the more common treatments of starch to produce dextrins, together with some properties of the resulting starches.

### CLASSIFICATION OF DEXTRINS

	<i>White Dextrins</i>	<i>Yellow or Canary Dextrins</i>	<i>British Gums</i>
<i>Manuf. Conditions</i>			
Usual catalyst	HCl	HCl	none or an alkali
Temperature, °C	79-121	149-218	135-218
Time, hrs.	3-8	6-18	10-20
<i>Product Characteristics</i>			
Color	white to light cream	buff to yellow or brown	buff to dark brown
Solubility (dispersibility), %	1-98	90-100	1-100
Useful diln., parts of water	2-5	1 or less	3-10

Refs

1, 16, 23, 24,  
29, 70

23

**Dextrin (page 2)**

**Specification:**

JAN-ID-232

The specification covers two types of corn dextrin: Type I—white, and Type II—yellow. These vary in composition as indicated by a wide difference in water solubility.

Molecular Weight:	variable (appreciably less than starch)	
Color:	white to dark brown	
Density, g./ml.:	1.0384	1
Melting Point:	decomposes	
Specific Heat, cal./g./°C at 90°C:	0.292	1
Hygroscopicity:	very deliquescent	20V3
Health Hazard:	non toxic	93
Safety Classifications:		
OSM:	not listed	
ICC:	no shipping label required	
Use in Pyrotechnics:	fuel and binder	

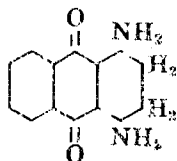
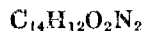
Dextrins have strong adhesive properties and are used mainly as pastes.

**Additional References:**

- 1) B. Brimhall, Ind. Eng. Chem. 36, 72 (1944)
- 2) J. Geerdes et al., J. Am. Chem. Soc. 79, 4209 (1957)
- 3) "Chemistry and Industry of Starch," R. W. Kerr, Ed., Academic Press, Inc., New York (1950)
- 4) G. M. Christensen and F. Smith, J. Am. Chem. Soc. 79, 4492 (1957)

**1,4-DIAMINO-2,3-DIHYDROANTHRAQUINONE**  
 (1,4-diamino-2,3-dihydro-9,10-dihydro-9,10-dioxoanthracene,  
 Violet A 100)

Structural Formula:



Specification No.:

MIL-D-3668

Covers one grade with a minimum purity of 87%.

Molecular Weight:

240.26

Color:

violet

Density, g./ml.:

(apparent)  $0.35 \pm 0.10$

Solubility:

soluble in 95% alcohol

Health Hazard: Some toxicity as indicated by the specification requirement that each container be conspicuously labelled: "CAUTION—Avoid skin contact or breathing of dust fumes. Provide adequate ventilation in work areas."

Safety Classifications:

OSM:

not listed

ICC:

not listed

Use in Pyrotechnics: To impart a violet color to burning smoke mixtures.

Refs.

82

Spec.

Spec.



## DIATOMACEOUS EARTH

(Infusorial earth, "Diatomite," fossil flour, Kieselguhr, Tripolite, Siliceous earth, Tripoli (a type of crystalline diatomite), "Celite," "Featherstone," "Filter-Cel," Super-Floss)

Diatomaceous earth is composed of the siliceous skeletons of diatoms, which are microscopic aquatic plants of the class Bacillarieae. These occur in great beds and are not earthy. Large deposits occur in the western part of the U.S. After being dug from open pits, the diatomite is prepared for commercial use usually by being heated to remove organic matter and treated with acids to remove iron. The individual diatoms occur in a great many forms and differ considerably in size. The average particle size varies from 1 to  $40\mu$  and the specific surface from about 7,050 to as much as 67,000 sq. cm./g. Chemically, diatomite is mainly silica (usually the  $\text{SiO}_2$  content is between 84 and 92%).

The impurities are highly variable and are usually Al and Fe oxides. The water content varies from 2 to 10%. The physical properties also vary over a wide range.

Diatomaceous earth is frequently used because of its highly absorptive character which is closely related to its specific surface. Oil absorption varies from 25 to 150 lbs. of oil per 100 lbs. of diatomite; water from one to four times the weight of diatomite. This porosity is a result of the fact that the shells of the diatoms are hollow.

Diatomite is a poor conductor of heat, electricity, and sound, and makes an excellent filter.

### Specification:

MIL-D-20550

The specification requires that the material be a naturally mined diatomaceous earth which has not been ignited.

$\text{SiO}_2$  content, %: 85.0 to 87.0

Organic matter, %: max 1.0

Linseed absorption, g. oil/100 g. material: 150 to 210

Normal color and form: white to light gray, to pale buff fine powder, varies with the nature of the impurities present

### Density g./ml.:

noncalcined 1.90

calcined and bleached, whitest grades 2.35

Apparent: 0.24 to 0.34

Spec. requirement: (max.) 0.3

Melting Point: Uncontaminated diatomaceous earth should melt at the temp. of fusion of silica, i.e.,  $1873^\circ\text{K}$  ( $1600^\circ\text{C}$ ). The average quality sinters at about  $1073^\circ\text{K}$  ( $800^\circ\text{C}$ ).

Specific Heat: cal./g./deg. at  $25^\circ\text{C}$ : 0.23

Hygroscopicity: —

Refs.

50V 3, 16.  
Addnl. Ref. 1

52V3, 29

Addnl. Ref. 2

50V10

Addnl. Ref. 2

Addnl. Ref. 2

**Diatomaceous Earth (page 2)**

Solubility Data: Insoluble in water, acids, and dilute alkalies. Resistant to most chemicals. Attacked by HF and slowly dissolved by hot aqueous caustic alkali. 29, 52

Health Hazard: Moderately toxic on inhalation. Under long exposure to high concentrations the dust may cause pulmonary fibrosis. 93, 29

Fire and Explosion Hazard: none mentioned

Use in Pyrotechnics: as an inert filler

**Additional References:**

- 1) "Clarifying Efficiency of Diatomaceous Filter Aids," A. B. Cummins, Ind. Chem., 34, 403 (1942)
- 2) "Diatomaceous Earth," R. Calvert, ACS Monograph No. 52, Chemical Catalogue Co., New York (1939)

# **DNBUTYL PHTHALATE**

(n-butylphthalate, dibutyl-o-phthallate, butyl phthallate,  
dibutyl-1,2-benzenedicarboxylate)

Formula:  $C_{16}H_{14}(COOC_4H_9)_2$  or  $C_{16}H_{22}O_4$

The industrial product made by the Commercial Solvents Corp. has the following properties: Purity, 99-100%; Boiling Range at 37 mm. press., 227-235°C; M.P. < -10°C; Flash Point, 347°F.

Specification No.: JAN-D-218  
Molecular Weight: 278.34  
Form: oily liquid  
Color: colorless  
Density, g./ml.: (liquid) 1.0465  
1.0427

Coefficient of Thermal Expansion: —

Heat of Formation, Kcal./mole at 18°C:

At constant pressures: -207.2

At constant volume: -199.6

Free Energy of Formation: —

Entropy: —

Melting Point: 238°K (-25°C)

Heat of Fusion: —

Boiling Point: 622°K (349°C)

613°K (340°C)

Transition Point: —

Heat of Sublimation: —

Heat Content or Enthalpy: —

Heat Capacity: —

Decomposition Temperature: —

Decomposition Products: —

Vapor Pressure:

Press mm.	1	10	40	100	400	760
Temp. °C	148.2	198.2	235.8	263.7	313.5	340

See also Addnl. Ref. 2

X-Ray Crystallographic Data: —

Hygroscopicity: —

Solubility Data: In water: 0.04 g./100 ml. at 25°C

Miscible in all proportions with alcohol, ether, acetone, benzene, and many organic liquids.

Refs.

1

1

1

Addnl. Ref. 2

Addnl. Ref. 1

29

31A

1

1

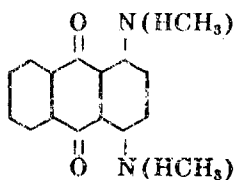
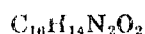
Dibutylphthalate (page 2)

Health Hazard: Low; ingestion can cause gastrointestinal disturbances.	29
Safety Classifications:	
OSM: Listed as substantially inert and presenting no particular fire or toxic hazard as used in Ordnance establishments.	
ICC: not listed	
Fire and Explosion Hazard: Combustible on exposure to heat or flame. Can react with oxidizing materials. To fight fire use water, foam, CO <sub>2</sub> , dry chemical, or CCl <sub>4</sub> .	75
Heat of Combustion, Kcal./mole at 20°C (H <sub>2</sub> O liquid):	1536.2
Flash Point, °F (closed cup):	315
(open cup):	335
Autoignition Temperature, °F:	757
Use in Pyrotechnics: As a solvent for nitrocellulose.	37, 71
Additional References:	
1) L. Médard, Mém. artillerie franç. 28. 476 (1954)	
2) "The Vapour Pressure of di-n-butylphthalate di-n-butylsebacate, Lauric Acid and Myristic Acid," E. Hammer and A. L. Lyderson, Chem. Eng. Sci. 1, 66 (1957)	

**1,4-BIS(METHYLAMINO)ANTHRAQUINONE**  
 (1,4-bis(methylamino)-anthraquinone; Duranol Brilliant Blue C,  
 Celliton (c) Fast Blue B; CI 61500, CI Disperse Blue 14)

Refs.

Structural Formula:



Specification No.:	MIL-D-21354
Molecular Weight:	266.30
Crystalline Form:	—
Color:	blue
Density:	—
Coefficient of Thermal Expansion:	—
Heat of Formation:	—
Free Energy of Formation:	—
Entropy:	—
Melting Point:	494-6°K (221-3°C)
Spec. min.:	482°K (209°C)
Heat of Fusion:	—
Boiling Point:	—
Transition Point:	—
Heat of Sublimation:	—
Heat Content or Enthalpy:	—
Heat Capacity:	—
Decomposition Temperature:	—
For DTA and TGA see Ref. 80	
Decomposition Products:	—
Vapor Pressure:	—
X-ray Crystallographic Data:	—
Absorption Spectra, see Ref. 66	
Hygroscopicity:	—
Solubility Data (mg./100 ml.),	
In water at 25°C:	<0.00002
at 80°C:	0.0002

Addnl. Ref. 1

Addnl. Ref. 2

Addnl. Ref. 3

1,4-Di(methylamino)anthraquinone (page 2)

(g./l. at 25°C) in $C_2H_5OH$ :	0.12	92
In ethyl acetate:	0.86	
In benzene:	1.9	
Health Hazard:	toxicity unknown	
The spec. requires that each container be conspicuously labeled, "Caution. Avoid skin contact or breathing of dust or fumes. Provide Adequate Ventilation."		
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard:	---	
Electrostatic Sensitivity:	---	
Use in Pyrotechnics:	to color smoke mixtures blue	
Additional References:		
1) C.A. 47, 870 (1953)		
2) J. Soc. Dyers Colourists 70, 68-77 (1954)		

# 4-DIMETHYLAMINOAZOBENZENE

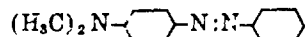
(Benzeneazodimethylaniline; N,N-dimethyl-p-phenylazoaniline;  
Sudan Yellow GGA, butter yellow; methyl yellow,  
C.I. 11020, C.I. Solvent Yellow 2)

Refs.

1, 29, 48, 48A

Structural Formula:

C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>



Specification No.:

XPA-PD-367 (Rev. 1)

The spec. requires a min. purity of 93%.

Molecular Weight:

225.30

Crystalline Form:

leaflets

1, 29

Color:

yellow

1

Density:

—

Coefficient of Thermal Expansion:

—

Heat of Formation:

—

Free Energy of Formation:

—

Entropy:

—

Melting Point:

388°K (115°C)

48

390°K (117°C)

Addnl. Ref. 1

Heat of Fusion:

—

Boiling Point:

—

Transition Point:

—

Heat of Sublimation, Kcal./mole:

28.9

Addnl. Ref. 2

Heat Content or Enthalpy:

—

Heat Capacity:

—

Decomposition Temperature:

For TGA see Ref. 80

Decomposition Products:

—

Vapor Pressure  $m\mu$  Hg between 86° and 108° =  $a + (b \times 10^3/T)$

Addnl. Refs.

1, 2

$a = 17.57 \pm 0.13$ ,  $b = -6.31 \pm 0.05$ ,  $T = \text{absolute temp.}$

Temp. °C	100	110	115
V.P. $\mu$	7.52	12.4	20.2

Addnl. Ref. 2

Energy of Volatilization, Kcal./mole

at 264–361°C (96% purity):

21.2

80

X-Ray Crystallographic Data:

—

Hygroscopicity:

—

Solubility Data (g./100 g.)

In water at 25°C:

0.00003

Addnl. Ref. 3

at 80°C:

0.0008

In pyridine:

about 28

88V15I

4-Dimethylaminoazobenzene (page 2)

In alcohol, benzene, chloroform, ether, petroleum ether, oils, and mineral acids:	soluble	29
Health Hazard:	may cause cancer	29, 84
The spec. requires that "Each container shall be conspicuously labeled: "CAUTION—Avoid skin contact or breathing of dust or fumes. Provide adequate ventilation."		
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard:		
Heat of Combustion, cal./mole. Cp:	1909.6	88V16
Cv:	1908.3	
Electrostatic Sensitivity:		
Use in Pyrotechnics:	to color smoke mixtures yellow	
Additional References:		
1) "The Vapor Pressures and Heats of Sublimation of p-Nitroaniline, NN-Dimethyl-p-nitroaniline, p-aminoazobenzene and NN-Dimethyl-p-aminoazobenzene," T. G. Majury, Chem. & Ind. 1956, 349		
2) "The Dyeing of Cellulose Acetate with Non-Ionic Dyes. III. Dyeing from the Vapour Phase," T. G. Majury, J. Soc. Dyers Colourists 72, 41 (1956)		
3) J. Soc. Dyers Colourists, 70, 68-77 (1954)		



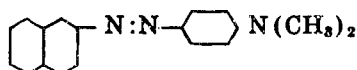
## 2-(4-DIMETHYLAMINOAZOPHENYL) NAPHTHALENE

(4- $\beta$ -naphthaleneazodimethylaniline;  
 $\beta$ -naphthaleneazo-4-dimethylaniline;  
N,N-Dimethyl-p-2-Naphthylazo Aniline)

Refs.

Structural Formula:

$C_{18}H_{17}N_3$



Specification No.:	MIL-D-3613
Molecular Weight:	275.36
Crystalline Form:	—
Color:	brownish-yellow
Density:	—
Coefficient of Thermal Expansion:	—
Heat of Formation:	—
Free Energy of Formation:	—
Entropy:	—
Melting Point:	445°K (172°C) 447°K (174°C)

Addnl. Ref. 1  
Addnl. Refs.  
2, 5

Heat of Fusion:	—
Boiling Point:	—
Transition Point:	—
Heat of Sublimation:	—
Heat Content or Enthalpy:	—
Heat Capacity:	—
Decomposition Temperature:	—
Decomposition Products:	—
Vapor Pressure:	—
X-Ray Crystallographic Data:	—

For Absorption Spectra see Addnl. Refs. 3, 4, 5

Hygroscopicity:	—
-----------------	---

Solubility Data (g. to dissolve 1 g. dye):

In toluene or $CCl_4$ :	70
In benzene:	soluble

Addnl. Refs.  
2, 3

Health Hazard:	—
----------------	---

Safety Classification:

OSM:	not listed
ICC:	not listed

**2-(4-dimethylaminoazophenyl) Naphthalene (page 2)**

Fire and Explosion Hazard: \_\_\_\_\_

Electrostatic Sensitivity: \_\_\_\_\_

Use in Pyrotechnics: \_\_\_\_\_ to color smoke mixtures  
yellow

**Additional References:**

- 1) "Condensation of aromatic amines with nitranilines. Preparation of azoamine compounds," M. Martynoff, *Compt. rend.* **227**, 1373 (1948)
- 2) "Zur Kenntniss der Diazoaminokörper," H. Goldschmidt and B. Bardach, *Ber.* **20**, 386 (1928)
- 3) "Some Azo Dyes in Non-Aqueous Solvents," C. May and H. Hunt, *Ind. Chem.* **20**, 386 (1928)
- 4) "Absorption spectra and structure of aminoazo derivatives," M. Martynoff, *Compt. rend.* **236**, 88 (1953); "Physical Properties of the Amincazobenzene Dyes. Absorption Spectra in Acid Solution," E. Sawicki, *J. Org. Chem.* **22**, 1084 (1957)
- 5) "Physical Properties of the Amincazobenzene Dyes. IX. Absorption Spectra in Alcohol and Acid Solution of Disazobenzene Dyes," E. Sawicki, *J. Org. Chem.* **23**, 532 (1958)

**DIPHENYLALANINE**  
(*n*-phenylalanine, Anilino benzene)

Formula:	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NH																	
Specification No.:	JAN-D-98																	
Molecular Weight:	169.22																	
Crystalline Form:	monoclinic	1																
Color:	colorless leaflets (darkens on exposure to light)	1																
Density, g./ml.:	(solid) 1.159	1																
Coefficient of Thermal Expansion:	—																	
Heat of Formation, Kcal./mole at 18°C:																		
at constant pressure:	-28.2	Addnl. Ref. 1																
at constant volume:	-31.7																	
Free Energy of Formation:	—																	
Entropy:	—																	
Melting Point:	326°K (53°C)	1																
Heat of Fusion, cal. (15°C)/g.:	25.2	1																
Boiling Point:	575°K (302°C)	1																
Transition Point:	—																	
Heat of Sublimation:	—																	
Heat Content or Enthalpy:	—																	
Heat Capacity:	—																	
Decomposition Temperature:	—																	
Decomposition Products:	—																	
Vapor Pressure:		1																
<table><tr><td>Press. mm.</td><td>1</td><td>10</td><td>40</td><td>100</td><td>400</td><td>760</td><td>M.P.</td></tr><tr><td>Temp. °C</td><td>108.3</td><td>157.0</td><td>194.3</td><td>222.8</td><td>274.1</td><td>302.0</td><td>52.9</td></tr></table>			Press. mm.	1	10	40	100	400	760	M.P.	Temp. °C	108.3	157.0	194.3	222.8	274.1	302.0	52.9
Press. mm.	1	10	40	100	400	760	M.P.											
Temp. °C	108.3	157.0	194.3	222.8	274.1	302.0	52.9											
X-Ray Crystallographic Data:																		
System	a	b	c	Axial Angle	Molecules/Unit Cell			1										
monoclinic	14.0	13.9	39.5	β = 91°30'	32													
Hygroscopicity:			—															
Solubility Data (g./100 ml.)								1										
In water at 25°C:			0.030															
In ethyl alcohol:			about 44															
In methyl alcohol:			57.5															
In ether:			very soluble															
In benzene and ligroin:			slightly soluble															
Health Hazard: Toxic on ingestion, inhalation, or skin absorption. Irritating to the mucous membranes.								12, 29										

**Diphenylamine (page 2)**

**Safety Classifications:**

OSM: Listed as substantially inert. Presents no particular fire or toxic hazard as used in Ordnance establishments.

Fire and Explosion Hazard: Dangerous; when heated to decomposition emits highly toxic fumes. Can react with oxidizing materials. Combustible.

To fight fire use water, CO<sub>2</sub>, dry chemicals, or CCl<sub>4</sub>.

Heat of Combustion, Kcal./mole at 20°C and 1 atm.: 1536.2

Specific Heat, cal. (15°)/g./°C, solid at 26°C: 0.337

liquid at 53°C: 0.464

Flash Point, °F (closed cup): 307

Autoignition Temperature, °F: 846

Electrostatic Sensitivity:

Use in Pyrotechnics:

as a stabilizer for  
nitrocellulose

12

67, 75

1

1

12, 67

12, 67

**Additional References:**

- 1) L. Médard, Mém. artillerie franç, 28, 478 (1954)

## ETHYLCELLULOSE

### (Cellulose Ethyl Ether)

Refs.

Formula:  $[C_6H_{10-x}O_5-x(OC_2H_5)_x]_n$

where x = no. of  $(OC_2H_5)$  groups and n = degree of polymerization

Specification No.:

MIL-E-10853B

The spec. covers 46.8-48.5% ethoxyl content or x = approximately 2.4-2.5, and lists two classes which vary in viscosity, ethoxyl content, ash content, and granulation: class I, 46.8-48.5%; class II, 47.1-48.1%.

Molecular Weight:

variable high

Crystalline Form:

(specification) amorphous granules

Color:

white

Density, g./ml.:

(solid) 1.09-1.17

60

Coefficient of Thermal Expansion:

—

Heat of Formation:

—

Free Energy of Formation:

—

Entropy:

—

Melting Point:

513°K + (240 + °C)

12

Ethyl cellulose with 48% ethoxyl content softens at 425-435°K

69

(152-162°C)

Heat of Fusion:

—

Boiling Point:

—

Transition Point:

Second order transition temperature, °C:

43

59

Heat of Sublimation:

—

Heat Content or Enthalpy:

—

Heat Capacity:

—

Decomposition Temperature:

—

For DTA and TGA see Ref. 33

Decomposition Products:

—

Vapor Pressure:

—

X-Ray Crystallographic Data:

—

Hygroscopicity:

—

Solubility Data (for 47% ethoxyl content): Soluble in ethyl acetate, ethylene, dichloride, benzene, toluene, xylene, butyl acetate, acetone, methanol, ethanol and  $CCl_4$ .

29

Health Hazard:

none mentioned

Safety Classifications:

OSM:

not listed

ICC:

not listed

**Ethylcellulose (page 2)**

Fire and Explosion Hazard: Combustible when exposed to heat or flame by chemical reaction with oxidizing agents. Flammability varies with ethoxyl content.	12, 60
Ignition Temperature of Dust Cloud, °C: 320	26
Burning Behavior: First melts and drips and drippings continue to burn. The flame is yellow with blue edges.	60
Commercial Types: A number of types of ethylcellulose are commercially available. These range from 44.5 to 49.0 + in ethoxyl content and from very low to highly viscous materials (5% concentration from 3 to 5000 + centipoises)	69
Electrostatic Sensitivity, minimum energy required for ignition of dust cloud by electric sparks (millijoules): 10	26
Use in Pyrotechnics: as a binding agent and retardant	17
Additional References:	
1) "Cellulose and Cellulose Derivatives," E. Ott et al., Eds., Interscience Publishers, Inc., New York (1954)	

# FERRIC OXIDE, Fe<sub>2</sub>O<sub>3</sub>

(Iron Oxide, Burned Ochre, Indian Red Rouge,  
Venetian Red, Red Chalk, Red Earth, Red Hematite, Red Stone,  
Persian Red, Persian Gulf Oxide, Colcothar, Iron Sesquioxide)

Refs.

1, 11, 16, 29

Percent Oxygen: 30.06  
Specification No.: JAN-I-706

The specification covers class 1, coarse, and class 2, fine.

Molecular Weight: 159.70  
Crystalline Form: hexagonal  
Color: reddish-brown to black  
Density, g./ml.: (solid) 5.24  
Coefficient of Thermal Expansion, linear:  $7 \times 10^{-6}$   
cubic:  $4 \times 10^{-5}$

1

1

54V13

See also Addnl. Ref. 2

Heat of Formation, Kcal./mole: -196.5

1, 9

See Table a

Free Energy of Formation, Kcal./mole: -177.9

8, 9

See Table a

## a. HEAT AND FREE ENERGY OF FORMATION OF Fe<sub>2</sub>O<sub>3</sub> (hematite, $\beta$ , $\gamma$ )

2

T, °K	$\Delta H$ (cal./mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . .	-196,800 ( $\pm 1300$ )	-177,400 ( $\pm 1500$ )
400 . . . . .	-196,400	-170,800
500 . . . . .	-195,800	-164,500
600 . . . . .	-195,200	-158,300
700 . . . . .	-194,500	-152,200
800 . . . . .	-193,800	-146,200
900 . . . . .	-193,000	-140,300
950 . . . . .	-192,800	-137,400
950 . . . . .	-192,600	-137,400
1000 . . . . .	-192,600	-134,500
1033 . . . . .	-193,100	-132,600
1033 . . . . .	-193,100	-132,600
1050 . . . . .	-193,000	-131,600
1050 . . . . .	-193,000	-131,600
1100 . . . . .	-193,000	-128,700
1179 . . . . .	-193,000	-124,100
1179 . . . . .	-193,400	-124,100
1200 . . . . .	-193,300	-122,800
1300 . . . . .	-193,000	-117,000

**Ferrie Oxide, Fe<sub>2</sub>O<sub>3</sub> (page 2)**

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
1400 . . . . .	-192,600	-111,100
1500 . . . . .	-192,400	-105,300
1600 . . . . .	-192,100	-99,500
1674 . . . . .	-191,900	-95,200
1674 . . . . .	-192,100	-95,200
1700 . . . . .	-192,100	-95,700
1800 . . . . .	-191,700	-88,000

**Phase Changes of Metal**

T.P., 1033°K; Δ H = 0 (Curie point)

T.P., 1179°K; Δ H = 210 cal./g.-atom

T.P., 1674°K; Δ H = 110 cal./g.-atom

**Free Energy Equations:**

Reaction	Range of Validity, °K
1) 2Fe (α) + 3/2 O <sub>2</sub> (g) = Fe <sub>2</sub> O <sub>3</sub> (hematite) Δ F <sub>T</sub> <sup>o</sup> = -200,000 - 13.84T log T - 1.45 (10 <sup>-3</sup> T <sup>2</sup> ) + 1.905 (10 <sup>5</sup> T <sup>-1</sup> ) + 108.28T	298.16-950
2) 2Fe (α) + 3/2 O <sub>2</sub> (g) = Fe <sub>2</sub> O <sub>3</sub> (β) Δ F <sub>T</sub> <sup>o</sup> = -202,960 - 42.64T log T + 7.85 (10 <sup>-3</sup> T <sup>2</sup> ) + .13 (10 <sup>5</sup> T <sup>-1</sup> ) + 188.48T	950-1033
3) 2Fe (β) + 3/2 O <sub>2</sub> (g) = Fe <sub>2</sub> O <sub>3</sub> (β) Δ F <sub>T</sub> <sup>o</sup> = -196,760 - 10.27T log T + .75 (10 <sup>-3</sup> T <sup>2</sup> ) - .30 (10 <sup>5</sup> T <sup>-1</sup> ) + 92.86T	1033-1050
4) 2Fe (β) + 3/2 O <sub>2</sub> (g) = Fe <sub>2</sub> O <sub>3</sub> (γ) Δ F <sub>T</sub> <sup>o</sup> = -193,200 - .39T log T - .13 (10 <sup>-3</sup> T <sup>2</sup> ) - .30 (10 <sup>5</sup> T <sup>-1</sup> ) + 59.96T	1050-1179
5) 2Fe (γ) + 3/2 O <sub>2</sub> (g) = Fe <sub>2</sub> O <sub>3</sub> (γ) Δ F <sub>T</sub> <sup>o</sup> = -202,540 - 25.95T log T + 2.87 (10 <sup>-3</sup> T <sup>2</sup> ) - .30 (10 <sup>5</sup> T <sup>-1</sup> ) + 142.85T	1179-1674
6) 2Fe (δ) + 3/2 O <sub>2</sub> (g) = Fe <sub>2</sub> O <sub>3</sub> (γ) Δ F <sub>T</sub> <sup>o</sup> = -192,920 - .85T log T - .13 (10 <sup>-3</sup> T <sup>2</sup> ) - .30 (10 <sup>5</sup> T <sup>-1</sup> ) + 61.21T	1674-1800

Entropy, cal./deg./mole at 298.16°K:

21.5

See Table b

Melting Point:

1838°K (1565°C)

Heat of Fusion:

—

Boiling Point:

—

Heat of Vaporization:

—

Transition Point:

α 950°K → β 1050°K γ

Heat of Transition, cal./mole:

α to β = 160; β to γ = 0

Heat of Sublimation:

—



Ferric Oxide, Fe<sub>2</sub>O<sub>3</sub> (page 3)

b. HEAT CONTENT AND ENTROPY OF Fe<sub>2</sub>O<sub>3</sub> (c)  
(Base, α-crystals at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	2750	7.91	1050 (γ) . . .	25,820	41.31
500 . . . . .	5770	14.64	1100 . . . . .	27,500	42.87
600 . . . . .	9010	20.54	1200 . . . . .	30,870	45.80
700 . . . . .	12,460	25.85	1300 . . . . .	34,250	48.51
800 . . . . .	16,130	30.75	1400 . . . . .	37,650	51.03
900 . . . . .	20,030	35.34	1500 . . . . .	41,070	53.39
950 (α) . . .	22,060	37.54	1600 . . . . .	44,540	55.63
950 (β) . . .	22,220	37.71	1700 . . . . .	48,100	57.79
1000 . . . . .	24,020	39.55	1800 . . . . .	51,880	59.95
1050 (β) . . .	25,820	41.31			

Fe<sub>2</sub>O<sub>3</sub> (α) :

Enthalpy:  $H_T - H_{298.15} = 23.49T + 9.30 \times 10^{-5}T^2 + 3.55 \times 10^{-8}T^3 - 9021$   
(0.1 percent; 298-950°K)

Heat Capacity:  $C_p = 23.49 + 18.60 \times 10^{-5}T - 3.55 \times 10^{-8}T^2$

Fe<sub>2</sub>O<sub>3</sub> (β) :

Enthalpy:  $H_T - H_{298.15} = 36.00T - 11,980$  (0.1 percent; 950-1050°K)

Fe<sub>2</sub>O<sub>3</sub> (γ) :

Enthalpy:  $H_T - H_{298.15} = 31.71T + 0.88 \times 10^{-5}T^2 - 8446$   
(0.1 percent; 1050-1800°K)

Heat Capacity:  $C_p = 31.71 + 1.76 \times 10^{-5}T$

Heat Capacity, cal./deg./mole: (solid) α = 25.0  
β = 36.0

Decomposition Temperature, °K: 1730

See also Ref. 54V13

Decomposition Products: (high temp.) Fe<sub>3</sub>O<sub>4</sub> + O<sub>2</sub>

Vapor Pressure: Difficult to vaporize. Contradictory data in the literature.

X-Ray Crystallographic Data:

	System	Space Group	a	Axial Angle	Molecules/ Unit Cell
(hematite)	hexagonal	D <sub>3d</sub> <sup>5</sup>	5.42	α = 55°17'	2
(magnetic)	cubic		8.30		

Hygroscopicity: —

Solubility Data: Insoluble in water; soluble in acids.

Health Hazard: none reported

M.A.C., mg /m.<sup>3</sup> (for fumes): 15

9

4

8

Addnl. Ref. 3

44V59B

1

50V7

25

**Ferrie Oxide,  $\text{Fe}_2\text{O}_3$  (page 4)**

Safety Classifications:	none listed
Fire and Explosion Hazard:	none listed
Electrostatic Sensitivity:	—
Use in Pyrotechnics:	as an oxidizer

**Additional References:**

- 1) "Health Hazards Associated with Welding," F. Hutchinson, Heating and Ventilating 41, 73 (1944)
- 2) C.A. 45, 9978 (1951) refers to Proc. Indian Acad. Sci. 33A, 245-249 (1951) where data are given.
- 3) C.A. 36, 4400 (1942)

FERROSOFERRIC OXIDE, $\text{Fe}_3\text{O}_4$		<i>Refs.</i>
(Iron (II, III) Oxide, Black Iron Oxide, Magnetite, Trüron Tetraoxide, Magnetic Iron Oxide, Ethiops Iron, Lodestone)		1, 2, 9
Percent Oxygen:	27.64	
Specification No.:	JAN-1-275	
Molecular Weight:	231.55	
Crystalline Form:	cubic	1
Color:	black to red-black	1
Density, g./ml.:	(solid) 5.18	1
Coefficient of Thermal Expansion, linear, 17-50°C:	$95.4 \times 10^{-6}$	54V13
(magnetite) cubic, 17-50°C:	$29 \times 10^{-6}$	
Heat of Formation, Kcal./mole at 298°K:	-267.0	1, 9
See Table a		
Free Energy of Formation, Kcal./mole at 298°K:	-242.4	1, 9
See Table a and Free Energy Equations		

a. HEAT AND FREE ENERGY OF FORMATION OF  $\text{Fe}_3\text{O}_4$  (magnetite  $\beta$ , 1) 2

T, °K	$\Delta H$ (cal./mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . .	-267,800 ( $\pm 1000$ )	-243,200 ( $\pm 1200$ )
400 . . . . .	-267,200	-234,900
500 . . . . .	-266,300	-226,900
600 . . . . .	-265,300	-219,100
700 . . . . .	-264,000	-211,500
800 . . . . .	-262,300	-204,100
900 . . . . .	-260,500	-197,000
900 . . . . .	-260,500	-197,000
1000 . . . . .	-260,800	-189,900
1033 . . . . .	-261,700	-187,600
1033 . . . . .	-261,700	-187,600
1100 . . . . .	-261,700	-182,800
1179 . . . . .	-261,700	-177,100
1179 . . . . .	-262,300	-177,100
1200 . . . . .	-262,200	-175,600
1300 . . . . .	-261,700	-168,400
1400 . . . . .	-261,300	-161,200
1500 . . . . .	-261,000	-154,100
1600 . . . . .	-260,800	-147,000
1674 . . . . .	-260,700	-141,700
1674 . . . . .	-261,000	-141,700
1700 . . . . .	-261,100	-139,800
1800 . . . . .	-261,100	-132,700
1803 . . . . .	-261,100	-132,500
1803 . . . . .	-272,200	-132,500
1870 . . . . .	-272,200	-127,300
1870 . . . . .	-239,200	-127,300
1900 . . . . .	-239,000	-125,800
2000 . . . . .	-238,200	-119,800

**Ferrosoferric Oxide, Fe<sub>3</sub>O<sub>4</sub> (page 2)**

**Phase Changes of Metal**

T.P., 1933°K; ΔH = 0 (Curie point)

T.P., 1179°K; ΔH = 210 cal./g.-atom

T.P., 1674°K; ΔH = 110 cal./g.-atom

M.P., 1803°K; ΔH = 3700 cal./g.-atom

**Free Energy Equations:**

Reaction	Range of Validity, °K	
1) 3Fe (α) + 2O <sub>2</sub> (g) = Fe <sub>3</sub> O <sub>4</sub> (magnetite)	298.16-900	2
ΔF <sub>T</sub> <sup>o</sup> = -268,310 + 5.87T log T - 12.45 (10 <sup>-3</sup> T <sup>2</sup> ) + .245 (10 <sup>5</sup> T <sup>-1</sup> ) + 73.11T		
2) 3Fe (α) + 2O <sub>2</sub> (g) = Fe <sub>3</sub> O <sub>4</sub> (β)	900-1033	
ΔF <sub>T</sub> <sup>o</sup> = -272,300 - 54.27T log T + 11.65 (10 <sup>-3</sup> T <sup>2</sup> ) + .245 (10 <sup>5</sup> T <sup>-1</sup> ) + 233.52T		
3) 3Fe (β) + 2O <sub>2</sub> (g) = Fe <sub>3</sub> O <sub>4</sub> (β)	1033-1179	
ΔF <sub>T</sub> <sup>o</sup> = -262,990 - 5.71T log T + 1.00 (10 <sup>-3</sup> T <sup>2</sup> ) - .40 (10 <sup>5</sup> T <sup>-1</sup> ) + 89.19T		
4) 3Fe (γ) + 2O <sub>2</sub> (g) = Fe <sub>3</sub> O <sub>4</sub> (β)	1179-1674	
ΔF <sub>T</sub> <sup>o</sup> = -276,990 - 44.05T log T + 5.50 (10 <sup>-3</sup> T <sup>2</sup> ) - .40 (10 <sup>5</sup> T <sup>-1</sup> ) + 213.52T		
5) 3Fe (δ) + 2O <sub>2</sub> (g) = Fe <sub>3</sub> O <sub>4</sub> (β)	1674-1803	
ΔF <sub>T</sub> <sup>o</sup> = -262,560 - 6.40T log T + 1.00 (10 <sup>-3</sup> T <sup>2</sup> ) - .40 (10 <sup>5</sup> T <sup>-1</sup> ) + 91.05T		
6) 3Fe (l) + 2O <sub>2</sub> (g) = Fe <sub>3</sub> O <sub>4</sub> (β)	1803-1874	
ΔF <sub>T</sub> <sup>o</sup> = -275,280 - 8.74T log T + 1.00 (10 <sup>-3</sup> T <sup>2</sup> ) - .40 (10 <sup>5</sup> T <sup>-1</sup> ) + 104.84T		
7) 3Fe (l) + 2O <sub>2</sub> (g) = Fe <sub>3</sub> O <sub>4</sub> (l)	1874-2000	
ΔF <sub>T</sub> <sup>o</sup> = -257,240 - 26.89T log T + 1.00 (10 <sup>-3</sup> T <sup>2</sup> ) - .40 (10 <sup>5</sup> T <sup>-1</sup> ) + 155.46		

Entropy, cal./deg./mole at 298°K:

35.0

1, 9

See Table b

Melting Point:

1867°K (1594°C)

9

Heat of Fusion, cal./mole:

33,000

2, 9

Boiling Point:

decomposes at  
260 ± 30°K (1737°C)

8

Heat of Vaporization:

Transition Point:

900°K (627°C)  
α → β

4

Heat of Transition, cal./mole:

0.0

Heat of Sublimation:

—

**b. HEAT CONTENT AND ENTROPY OF Fe<sub>3</sub>O<sub>4</sub>(c)  
(Base, α-crystals at 298.15°K)**

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	3990	11.48	1100 . . . . .	40,150	62.81
500 . . . . .	8320	21.12	1200 . . . . .	44,950	66.99
600 . . . . .	13,660	29.75	1300 . . . . .	49,750	70.83
700 . . . . .	18,340	37.88	1400 . . . . .	54,550	74.39
800 . . . . .	24,260	45.77	1500 . . . . .	59,350	77.70
900 (α) . . . .	30,550	53.18	1600 . . . . .	64,150	80.80
900 (β) . . . .	30,550	53.18	1700 . . . . .	68,950	83.71
1000 . . . . .	35,350	58.24	1800 . . . . .	73,750	86.45

**Ferrosoferric Oxide,  $\text{Fe}_3\text{O}_4$  (page 3)**

$\text{Fe}_3\text{O}_4 (\alpha) :$

Enthalpy:  $H_T - H_{298.15} = 21.88T + 24.10 \times 10^{-3}T^2 - 8666$   
(0.5 percent; 298-900°K)

Heat Capacity:  $C_p = 21.88 + 48.20 \times 10^{-3}T$

$\text{Fe}_3\text{O}_4 (\beta) :$

Enthalpy:  $H_T - H_{298.15} = 43.00T - 12,650$  (0.1 percent; 900-1800°K)

Heat Capacity, cal./deg./mole: (solid)  $\beta$ , 48.00

Decomposition Temperature, °K:  $2060 \pm 30$

Stable at red heat. Begins to decompose in a current of N at over 1300°.

Decomposition Products: —

Vapor Pressure: —

**X-Ray Crystallographic Data:**

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Molecules/Unit Cell</i>
cubic	$O_h^1$	8.37	8

Solubility Data: Slightly soluble in acid; insoluble in alcohol and ether.

Health Hazard: none reported

M.A.C., mg./in.<sup>3</sup> (for fumes): 15

Safety Classifications: —

Fire and Explosion Hazard: —

Electrostatic Sensitivity: —

Use in Pyrotechnics: as an oxidizer

**Additional Reference:**

- 1) "Health Hazards Associated with Welding," F. Hutchinson, Heating and Ventilating 41, 73 (1944)

# FERROUS SULFIDE, FeS

(Iron Monosulfide, Iron Proto-Sulfide, Pyrrhotite)

Refs.

Specification No.:	JAN-F-279	
The spec. covers one grade and two classes. Class A requires a min. of 99.9% through a No. 100 Standard Sieve and Class B requires that the FeS be furnished in pieces capable of passing through a sieve having openings 1-in. square.		
Molecular Weight:	87.92	
Crystalline Form:	hexagonal	1
Color:	black-brown (colorless when pure)	1, 79
Density, g./ml.:	(solid) 4.84	1
Coefficient of Thermal Expansion (pyrrhotite) at 40°C:		
In direction of principal axis:	.00000235	54
Perpendicular:	.00003120	
Heat of Formation, Kcal./mole at 298°K:	(c) $\alpha$ , -22.72	1, 9
	$\beta$ , -21.35	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(c) $\alpha$ , -23.32	1, 9
Entropy, cal./deg./mole at 298°K:	16.1	1, 9
See following table		
Melting Point:	1468°K (1195°C)	4, 7
Heat of Fusion, cal./mole:	$\beta$ , 5000	7
	$\gamma$ , 7730	4
Boiling Point:	decomposes	1
Transition Point:	$\alpha \xrightarrow{411^\circ\text{K}} \beta \xrightarrow{598^\circ\text{K}} \gamma$	
Heat of Transition, cal./mole:	$\alpha \xrightarrow{570^\circ\text{K}} \beta \xrightarrow{120^\circ\text{K}} \gamma$	4

## HEAT CONTENT AND ENTROPY OF FeS(c, l) (Base, $\alpha$ -crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350 . . . . .	710	2.19	1100 . . . . .	12,680	21.35
500 . . . . .	1470	4.21	1200 . . . . .	14,150	22.63
411 ( $\alpha$ ) . . .	1640	4.63	1300 . . . . .	15,680	23.86
411 ( $\beta$ ) . . .	2210	6.02	1400 . . . . .	17,260	25.03
500 . . . . .	3760	9.43	1468 ( $\gamma$ ) . . .	18,350	25.79
598 ( $\beta$ ) . . .	5460	12.53	1468 (l) . . .	26,080	31.05
598 ( $\gamma$ ) . . .	5580	12.73	1500 . . . . .	26,620	31.42
600 . . . . .	5610	12.79	1600 . . . . .	28,320	32.51
700 . . . . .	7020	14.96	1700 . . . . .	30,020	33.54
800 . . . . .	8430	16.84	1800 . . . . .	31,720	34.51
900 . . . . .	9840	18.50	1900 . . . . .	33,420	35.43
1000 . . . . .	11,250	19.99	2000 . . . . .	35,120	36.31

**Ferrous Sulfide, FeS (page 2)**

FeS( $\alpha$ ):		
Enthalpy: $H_T - H_{298.15} = 5.19T + 13.20 \times 10^{-5}T^2 - 2721$ (0.8 percent; 298–411°K)		
Heat Content: $C_p = 5.19 + 26.40 \times 10^{-5}T$		
FeS( $\beta$ ):		
Enthalpy: $H_T - H_{298.15} = 17.40T - 4944$ (0.1 percent; 411–598°K)		
FeS( $\gamma$ ):		
Enthalpy: $H_T - H_{298.15} = 12.20T - 1.19 \times 10^{-5}T^2 - 2138$ (0.3 percent; 598–1468°K)		
Heat Content: $C_p = 12.20 + 2.38 \times 10^{-5}T$		
FeS(l):		
Enthalpy: $H_T - H_{298.15} = 17.00T + 1120$ (0.1 percent; 1468–2000°K)		
Heat Capacity, cal./deg./mole:	( $\alpha$ ) 13.1 ( $\beta$ ) 17.4 (liquid) 17.00	4, 9
Decomposition Temperature: In a vacuum, dissociation starts at about 1100°C and is complete at 1600°C.		79V2
Decomposition Products:	Fe + S	
Vapor Pressure:	—	
X-Ray Crystallographic Data:		
System	Space Group	Molecules/Unit Cell
hexagonal	$C_{6v}$	2
	$a$	
	3.43	
	$c$	
	5.79	
Hygroscopicity:		1
Solubility Data: In water: .00062 g./100 ml. at 18°C. Soluble in acids with evolution of H <sub>2</sub> S. Insoluble in ammonia.		1
Health Hazard:	slight (ordinary temp.)	12
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard: Dangerous when heated to decomposition, due to the highly toxic fumes of oxides of sulphur. On contact with moist acids poisonous hydrogen sulphide evolves which can form explosive mixtures with air. May react violently with powerful oxidizers.		12
Use in Pyrotechnics:	as a fuel	

## GRAPHITE

(Plumbago, Black Lead, Mineral Carbon,  
Silver Lead, Carburet of Iron)

Graphite occurs naturally as a mineral and is also made artificially by heating carbon, usually coal, in an electric furnace. Natural graphites are of three general types: flake, crystalline (plumbago), and amorphous. The artificial product is purer than the natural. Graphite is marketed in a number of grades based on purity, electrical resistance, and fineness. In an inert atmosphere graphite can be kept at 3000°C without change, but in air combines with oxygen above 600°C. The hardness of natural graphite is less than that of talc, which is 1 on Moh's scale. Graphite is a good conductor of heat and electricity.

Specification No.:

JAN-G-155

The spec. covers four grades: grades 1 and 3 are manufactured; 2 and 4 are natural. They differ in purity, the natural being less pure and containing up to 6% max. of silica vs. 0.6% for the manufactured material. Natural graphite is used in pyrotechnics.

Molecular Weight:	12.011	
Crystalline Form:	hexagonal	1
Color:	black	1
Density, g./ml.:	(solid) 2.25	1
Coefficient of Thermal Expansion, linear at 40°C:	$7.86 \times 10^{-6}$	1, 63
Heat of Formation, Kcal./mole at 298°K:	(gas) -170.890	5
Free Energy of Formation, Kcal./mole at 298°K:	(gas) -160.040	5
Entropy, cal./deg./mole at 298°K:	(gas) 37.76 (solid) 1.37	3, 4, 5 5
See following table		
Melting Point:	sublimes	
Heat of Fusion, cal./mole:	8000	Addnl. Ref. 4
Boiling Point:	4000°K (3727°C)	5
Transition Point (sublimation temp.)	4620°K (4347°C)	1
Heat of Sublimation, Kcal./mole, to ideal		
monatomic gas:	170	5
to diatomic and triatomic gas:	200	
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 251	
See equation below table	(gas, ideal)	
	monatomic, 1559	5
	diatomic, 2096	
	triatomic, 2541	

Refs.

16, Addnl.  
Ref. 1



## Graphite (page 2)

HEAT CONTENT AND ENTROPY OF C (graphite)  
(Base, crystals at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400	250	0.72	1800	7330	7.78
500	570	1.43	1900	7920	8.10
600	950	2.12	2000	8530	8.41
700	1370	2.77	2100	9130	8.70
800	1830	3.38	2200	9740	8.99
900	2320	3.95	2300	10,350	9.26
1000	2820	4.48	2400	10,970	9.52
1100	3340	4.98	2500	11,600	9.78
1200	3880	5.45	2750	13,170	10.38
1300	4430	5.89	3000	14,770	10.93
1400	4990	6.30	3250	16,390	11.45
1500	5560	6.70	3500	18,020	11.93
1600	6150	7.08	3750	19,660	12.39
1700	6740	7.44	4000	21,310	12.81

## C(graphite):

Enthalpy:  $H_T - H_{298.15} = 4.03T + 0.57 \times 10^{-3} T^2 + 2.04 \times 10^5 T^{-1} - 1936$   
(3.0 percent; 298-2500°K)Heat Capacity:  $C_p = 4.03 + 1.14 \times 10^{-3} T - 2.04 \times 10^5 T^{-2}$ 

Heat Capacity, cal./deg./mole:

(solid) 2.07 (gas) 4.98

4, 5, 9

See equation below table

Decomposition Temperature: —

Decomposition Products: —

Vapor Pressure:

Press. mm.	1	10	40	100	400	760
Temp. °C	3586	3946	4196	4373	4660	4827

1

## X-Ray Crystallographic Data:

System	Space Group	a	c	Molecules/Unit Cell
hexagonal	D <sub>6h</sub> <sup>4</sup>	2.455	6.99	4

1

Hygroscopicity: —

Solubility Data: Insoluble in water, acids and alkalies. Soluble in molten iron.

1

Health Hazard: Dust can irritate eyes.

12

Safety Classifications:

OSM:

not listed

ICC:

not listed

Fire and Explosion Hazard: —

**Graphite (page 3)**

Electrostatic Sensitivity:

Heat of Combustion, Kcal./g.:

7.900

Use in Pyrotechnics:

as a lubricant; to improve  
bonding under pressure

1

**Additional References:**

- 1) "Industrial Carbon," C. L. Mantell, D. Van Nostrand Co., Princeton, N. J. (1946)
- 2) "The Specific Heat of Graphite from 13° to 300°K," W. De Sorbo and W. W. Tyler, Chem. Physics 21, 1660 (1953); see also Ref. 63
- 3) Ref. 64
- 4) "Vapor Pressure and Heat of Vaporization of Graphite," A. L. Marshall and F. J. Norton, J. Am. Chem. Soc. 55, 432 (1933)
- 5) For X-Ray structure see also "The Synthesis of Diamond," H. T. Hall, J. Chem. Ed. 38, 484 (1961)

## GUM ARABIC

(Gum Preservative, Gum Acacia)

Refs.

Gum arabic is the dried gummy extraction obtained from acacia trees. The gum is produced when the trees are in an unhealthy condition. Most of the gum comes from the Sudan and West Africa. Today tapping is widely used. The gum exudes as droplets or "tears" which gradually harden on exposure to the atmosphere. These "tears" are 0.75 to 3 in. in diameter. After the "tears" are removed the tree continues to exude gum from the wound. For the better grades the cleaned gum is hand picked to remove extraneous material. Some gum is bleached by exposure to the sun for several weeks. The gum is available in several grades: natural, cleaned and sifted, bleached and dust.

16, 23, 29, 61

In addition to the more common names of gum arabic, gum preservative, and gum acacia, other names relating to the color or grade or to the local area are used so that there is a great deal of confusion concerning the relationship among the name, the actual gum and the species of acacia from which the gum is derived. As usually shipped the gum contains about 15% moisture. Its aqueous solution is slightly acid.

Gum arabic has been used as an adhesive since ancient times. It is a good emulsifying agent.

See also Addnl. Refs. 1, 2, 3

Specification:

JJJ-G-821

Molecular Weight: Variable high; probably in the range of 100,000 to 200,000.

See Structure below

Density, g./ml.:

1.3-1.4  
1.35-1.49

1  
29

Vapor Pressure:

—

X-Ray Crystallographic Data:

—

Hygroscopicity: Poor resistance to water.

29, 60

Solubility Data: Soluble in hot or cold water; oil and most organic solvents; aqueous alcohol up to about 60% alcohol; glycerol and propylene glycol.

1, 23, 29

Safety Classifications:

OSM:

not listed

ICC:

not listed

Health Hazard: When injected intravenously may cause allergic reactions, kidney and liver damage.

29

Fire and Explosion Hazard:

combustible

Electrostatic Sensitivity:

—

Chemical Structure:

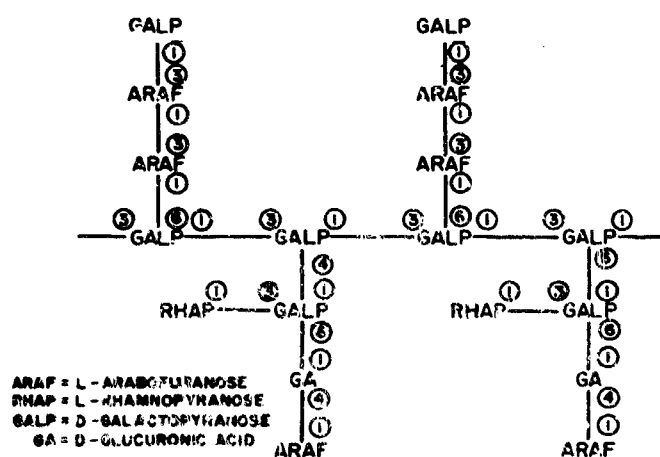
Gum arabic from different sources contains the same sugars, but their proportions vary considerably, as shown by the following table:

Gum Arabic (page 2)

MOLAR RATIO OF CARBOHYDRATE COMPONENTS IN  
VARIOUS ACACIA GUMS

Gum Source	Approximate Molar Ratio			
	D-Galactose	L-Arabinose	L-Rhamnose	D-Glucuronic Acid
Gum arabic	3	3	1	1
Acacia mollissima	5	6	1	1
Acacia cyanophylla	11	2	5	5
Acacia karroo	25	22	1	6
Acacia verec	4	2	1	1
Acacia pycnantha	65	27	2	4

A number of complex structures have been proposed not only for gum from different sources but also from the same source. Hydrolysis of gum arabic yields four different sugars, as shown in the table above, which together make up the basic gum arabic molecule. Because the proportions of these sugars vary with the source of the gum, no single formula can have any real significance. The following proposed structure indicates the complex nature of the gum:



PROPOSED STRUCTURE FOR GUM ARABIC

Use in Pyrotechnics:

as a fuel, bonding agent,  
adhesive, and retardant

Additional References:

- 1) Ref. 70
- 2) "Natural Plant Hydrocolloids," Ind. & Eng. Chem., Eds., Advances in Chemistry Series, No. 11, American Chemical Society, Washington, D.C. (1954)
- 3) "The Structure of Acacia Senegal Gum—Part I. Nature of the Sugars Present and Structure of the Aldobiuronic Acid," S. Mukherjee and A. N. Shivastava, J. Am. Chem. Soc. 80, 2536 (1958)

## GUM TRAGACANTH

Gum tragacanth is the dried gummy exudate obtained from several varieties of the shrub-like plants of the *Astragalus* family, which grow in the semi-desert and mountainous areas of Turkey, Iran, and Syria. The gum exudes spontaneously and hardens on exposure to the air either in the form of short (2-4 in.) ribbons which are flat, flexible and opaque, or in thick brittle flakes (0.5-2 in.), depending on the particular species of plant. The supply is increased by making incisions in the shrubs. The gum is sorted into five grades; the best grades being the lightest colored of the longest ribbons or largest flakes.

Chemically, gum tragacanth is a complex mixture of polysaccharides. On hydrolysis D-galacturonic acid, D-galactose, L-fucose, D-xylose, and L-arabinose are obtained. Gum tragacanth is about 60-70% insoluble in water, but swells to form a gel which is regarded as bassorin ( $C_{11}H_{20}O_{15}$ ). The water soluble portion which gives a colloidal hydrosol with water is called tragacanthin. It consists of a ring of three molecules of glucuronic acid and 1 molecule of arabinose with a side chain of two molecules of arabinose.

Gum tragacanth in solution has the properties of a partially cross-linked polymer, in that a small portion is soluble while the greater portion remains as a swollen gel or gel-like dispersion. When properly preserved, gum tragacanth forms stable solutions over long periods of time in either cold or warm storage.

A study of the infrared spectra of a wide variety of gums showed that the different samples of any one type of gum have essentially the same type of spectrum. Tragacanth shows a strong carbonyl absorption at about  $5.75\mu$ . The differences among the various infrared spectra are sufficiently definite to serve as a means of identification and classification.

An analysis of a representative sample of gum tragacanth shows the following percentages:

Moisture	10	Ash	3
Starch	3	Tragacanth	70
		(swelling part)	
Cellulose	4	Araban	10
		(soluble part)	

Viscosity is the most important property in evaluating gum tragacanth. It is the most direct measure of the uniformity and quality of the gum. To obtain maximum viscosity, the gum is crushed and soaked overnight. The dispersion is then stirred for 15-30 minutes. For powdered gums, it is best to disperse the gums in small amounts of ethanol or glycerol before the addition of water. Heat is not recommended for faster dissolution or increased viscosity. Viscosity is also decreased by adding acid, alkali, and NaCl.

Specification No.:

JAN-G-96

Solubility Data: Partly soluble in water. Films cast from aqueous solutions of gum tragacanth are unaffected by organic solvents such as acetone, ethanol,  $CCl_4$ , xylene, and toluene. When painted with solutions of basic or neutral lead acetate, these films also become insoluble in water.

Health Hazard: Nontoxic. Used in pharmaceutical compounding.

Safety Classifications:

OSM:

not listed

ICC:

not listed

Fire and Explosion Hazard:

combustible

Use in Pyrotechnics:

fuel; bonding agent

Additional References:

- 1) "Natural Plant Hydrocolloids," Ind. & Eng. Chem., Eds., Advances in Chemistry Series No. 11, American Chemical Society, Washington, D.C. (1954)

Refs.

23, 29, 61, 70  
Addnl. Ref. 1

# HEXACHLOROBENZENE, C<sub>6</sub>Cl<sub>6</sub>

(Perchlorobenzene)

Specification No.:	JAN-H-257	
Molecular Weight:	284.80	
Crystalline Form:	monoclinic or rhombic prisms	1
Color:	colorless	1
Density, g./ml.:	(solid) 2.044 (rhomb.)	1
Coefficient of Thermal Expansion:	---	
Heat of Formation, Kcal./mole at 25°C:	-31.5 ± 0.3	Addnl. Ref. 1
Free Energy of Formation, Kcal./mole at 298°K:	+ 3 ± 1.0	Addnl. Ref. 2
Entropy, cal./deg./mole at 298°K:	62.20	Addnl. Ref. 2
Melting Point:	500°K (227°C)	1
Heat of Fusion:	---	
Boiling Point:	599°K (326°C)	1
Transition Point, rhombic to triclinic:	316.7°K (43.6°C)	Addnl. Ref. 3
triclinic to cubic:	345°K (72°C)	76
Heat of Sublimation:	---	
Heat Content or Enthalpy:	---	
Heat Capacity, cal./deg./mole at 298°K:	(solid) 48.11	Addnl. Ref. 2
Decomposition Temperature: For DTA see Addnl. Ref. 4		
Decomposition Products:	---	
Vapor Pressure:		

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	114.4	166.4	206.0	235.5	283.5	309.4	230

## X-Ray Crystallographic Data:

System	Space Group	a	b	c	Axial Angle	Molecules/Unit Cell
monoclinic	C <sub>2h</sub>	8.07	3.84	16.61	β = 116°52'	2
		8.10	3.86	16.68		

Hygroscopicity:	---	
Solubility Data: In water:	insoluble	1
In alcohol:	insoluble cold, very soluble hot	
In benzene:	soluble hot	
In ether:	very slightly soluble	
Health Hazard: May produce mild skin irritation on prolonged contact. OSM states that it presents no particular toxic hazard as used in Ordnance establishments. Severely toxic on ingestion or inhalation.		29, 14, 93
M.A.C., mg./m. <sup>3</sup>	0.5	17

**Hexachlorobenzene, C<sub>6</sub>Cl<sub>6</sub> (page 2)**

**Safety Classifications:**

OSM: Inert and presents no particular fire hazard in Ordnance establishments.

ICC: No shipping label required.

Manufacturing Chemists Assn. requires a warning label.

22

**Fire and Explosion Hazard:** Slight when exposed to heat or flame. Flash point 468°F. Dangerous when heated to decomposition because of emission of highly toxic fumes. To fight fire use CO<sub>2</sub>, dry chemical, or carbon tetrachloride.

12

**Heat of Combustion, at 20°C and 1 atm., Kcal./mole.**

(water liquid): 509.0

1

25°, cal./g. (water liquid): 1995.3

Addnl. Ref. 1

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:**

as a color intensifier  
and chlorine donor in  
white smokes

17

**Additional References:**

- 1) "Heats of Combustion of Some Organic Compounds Containing Chlorine," G. C. Sinke and D. R. Stull, *J. Phys. Chem.* **62**, 397 (1958)
- 2) "The Heat Capacities of Hexachlorobenzene and Pentachlorophenol from 15° to 300°K," D. L. Hildenbrand et al., *J. Phys. Chem.* **62**, 958 (1958)
- 3) "The Vapor Pressures, Latent Heats of Sublimation and Transition Points of Solid Hexachloroethane," K. J. Ivir and F. S. Dainton, *Trans. Faraday Soc.* **43**, 32 (1947)
- 4) "Pre-Ignition and Ignition Reactions of the Pyrotechnic System Zn - C<sub>6</sub>Cl<sub>6</sub> - KClO<sub>4</sub>," S. Gordon and C. Campbell, Reinhold Publishing Company, New York (1955)

# HEXACHLOROETHANE, CCl<sub>3</sub>·CCl<sub>3</sub>

(Can be Hexachloride, Perchloroethane Carbon Trichloride)

Specification No.: JAN-H-235  
The spec. covers one grade and two classes: class a, unground, and class b, ground.

Molecular Weight: 236.76  
Crystalline Form: rhombic, tablets from alcohol or ether  
rhombic, triclinic or cubic  
Color: colorless to yellowish-white

Density, g./ml.: (solid) .091

Coefficient of Thermal Expansion: —

Heat of Formation, Kcal./mole at 298°K: (gas) -48

Free Energy of Formation, Kcal./mole at 298°K: —

Entropy, cal./deg./mole at 298°K: 91.97

See table below

Melting Point: (sublimes)  
186.6°K (-86.5°C)

Heat of Fusion, Kcal./mole: —

Boiling Point: (sublimes)  
457.5°K (184.4°C)

Heat of Vaporization, cal./g.: approx. 43

Transition Point: sublimes at  
457.6°K (184.5°C)  
rhombic→triclinic  
43.6°K (-229.5°C)  
triclinic→cubic  
72°K (-201°C)

Heat of Sublimation, Kcal./mole: 12.2

Heat Content or Enthalpy:

See table below

Heat Capacity, cal./deg./mole: (solid) 41

See table below

## ENTROPY, ENTHALPY, AND HEAT CAPACITY

Temp. °K	Entropy cal./deg./mole	Enthalpy cal./mole	Heat Capacity cal./deg./mole
273.16 . . . .	91.97	0	31.52
300 . . . . .	94.98	862	32.74
500 . . . . .	113.23	8052	38.32
800 . . . . .	132.02	20080	41.31
1000 . . . . .	141.33	28430	42.13
1200 . . . . .	149.06	36910	42.59
1500 . . . . .	158.061	49750	42.93

Refs.

1, 12

1

12

1

1

9

Addnl. Ref. 3

12

9

52V1

9

9

Addnl. Ref. 3



**Hexachloroethane CCl<sub>3</sub>·CCl<sub>3</sub> (page 2)**

Heat Capacity equation for the range 0-1200°C:

$$C_p^\circ = a + b(t) + c(t^2) + d(t^3) \quad (t = ^\circ K)$$

$$a = 31.820; b \times 10^3 = 3.6396; c \times 10^5 = 4.2031; d \times 10^8 = 1.6198$$

Decomposition Temperature: For DTA and TGA see Ref. 33

Decomposition Products: Heated in a stream of air at about 550-600°C it is completely converted to C<sub>2</sub>Cl<sub>4</sub> and CCl<sub>4</sub>. 50

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	31.7	73.5	102.3	124.2	168.8	185.6	186.6

X-Ray Crystallographic Data:

System	Space Group	a	b	c	Molecules/Unit Cell
rhomb.	V <sub>h</sub> <sup>16</sup>	11.51	10.14	6.39	4
cubic		7.43			2

Hygroscopicity:

Solubility Data: In water:

insoluble

1, 29

In benzene, chloroform, oils:

soluble

In alcohol and ether:

very soluble

Health Hazard: May be moderately irritating to the skin and mucous membranes. In high concentrations it has a narcotic effect, and may damage the liver and kidneys. MLD, i.v. (in dogs) 325 mg./kg. Has an odor similar to that of camphor. Moderately toxic locally, on ingestion, and inhalation. 12, 29, 93

Safety Classifications:

OSM: Substantially inert and presents no particular fire or toxic hazard as used in Ordnance establishments.

Fire and Explosion Hazards: Relatively inert, but when heated to decomposition it emits highly toxic fumes of chlorides. Dehalogenation by heating with alkalis and metals, produces explosive chloracetylenes. 12

Nonflammable

53V1

Electrostatic Sensitivity:

Heat of Combustion, Kcal./mole at 20°C and 1 atm.: 110.0

1

Triple Point, °C:

186.0

50V3, 54V3

Use in Pyrotechnics:

as a chlorine carrier  
for screening smoke  
compositions

Additional References:

- 1) E. H. Wibenga, Zeit. anorg. Chem. 225, 33 (1935)
- 2) K. J. Ivin and F. S. Dainton, Trans. Faraday Soc. 43, 32 (1947)
- 3) "Thermodata for Petroleum Chemicals," K. A. Kobe and R. H. Harrison, Petrol. Refiner 36, 155 (1957)

**INDANTHRENE GOLDEN YELLOW G.K. (spec. name)**

(HVT Golden Yellow; Indanthrene Golden Yellow GKAC;  
dibenzo(a,h)pyrene-7,14-dione; 3,4,8,9-dibenzopyrene-7,14-dione;  
listed in the Ring Index as No. 3654,  
C.I. 59100, C.I. Vat Yellow 4)

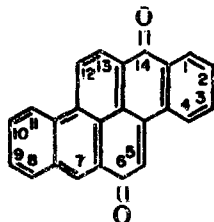
Structural Formula:

$C_{24}H_{12}O_2$

*Refs.*

90, 48A

84



Specification No.:

MIL-D-50029

Molecular Weight:

332.3

Crystalline Form:

—

Color:

golden yellow

Melting Point:

658°K (385°C)

Solubility Data: In dilute NaOH,  $H_2SO_4$ , quinoline, nitrobenzene, xylene,  
tetrahydronaphthalene:

soluble

In acetone, benzene, chloroform, pyridine, toluene:

slightly soluble

Health Hazard: Some toxicity as indicated by the spec. requirement that "Each  
container shall be conspicuously labeled: CAUTION—Avoid skin contact;  
use with adequate ventilation!"

Use in Pyrotechnics:

to color smoke mixtures  
yellow

88V7 II

88V7 II

38V7 II,  
48A

## KEROSENE

(Kerosine, Coal Oil, Lamp Oil, Fuel Oil No. 1)

Kerosene is a variable mixture of petroleum hydrocarbons, chiefly of the methane series, 10 to 16 atoms of carbon per molecule.

Kerosene is the light oily liquid obtained in the fractionation of petroleum. It is the fraction which is obtained by the overhead distillation of crude petroleum in the 174° and 180° range. It contains hydrocarbons in the range  $C_{10}H_{22}$  to  $C_{16}H_{34}$ . Some commercial kerosenes may include distillates up to 325°C and a specific gravity as high as 0.850. In Pennsylvania, kerosene is defined as having a flash point above 114°F, with not over 10% distillable at 175° and not over 45% up to 200°C. A typical analysis of the kerosene from a midcontinent crude includes n-dodecane, alkyl derivatives of benzene, naphthalene, 1- and 2-methyl-5, 6, 7, 8-tetrahydronaphthalene.

The fraction obtained by distillation is decolorized by washing with fuming  $H_2SO_4$ , followed by treatment with sodium plumbite solution and sulfur (Doctor sweetening).

Specification No.:	VV-K-211C	
Normal Color and Form:	pale yellow to white oily liquid	1
Density, g./ml.:	(liquid) at 60°F, 0.819	1
Coefficient of Thermal Expansion:	—	
Melting Point, °F:	-76	14
Boiling Point, °F:	410-572	14
Decomposition Temperature:	—	
Decomposition Products:	—	
Solubility Data: In water:	insoluble	
With other petroleum solvents:	miscible	29
Health Hazard: Toxic when ingested or inhaled; causes local irritation, drowsiness, collapse and coma, and may damage the heart, liver, and kidneys.		12, 29
Safety Classifications:		
Underwriters Laboratory Classification:	40	12
OSM:	flammable liquid	
ICC:	not listed	
U.N.:	inflammable liquid	
The ICC does not classify kerosene as a flammable liquid because the flash point is above the maximum for this classification.		

*Refs.*

1, 11, 16

12, 16, 29, 53

29

**Kerosene (page 2)**

<b>Fire and Explosion Hazard:</b> Ignites when exposed to heat or flame. Can also explode in air. To fight fire use foam, CO <sub>2</sub> , dry chemical, CCl <sub>4</sub> .		14
<b>Flash point:</b>	100-165°F	75
<b>Autoignition temperature:</b>	490°F	
	395°C	71
<b>Explosive limits (% by vol. in air):</b>	1.16-8.0	26, 75
<b>Explosive limits in closed vessel:</b>	0.7-5	
<b>M.A.C., parts per million in air for an 8-hr. day:</b>	500	14
<b>Heat of Combustion (for kerosene with sp. gr. 0.819)</b>		
<b>cal./g.:</b>	11,006	71
<b>Use in Pyrotechnics:</b> To prevent dusting in Green Smoke composition I and in Violet Smoke composition II. See specifications MIL-STD-516 and 522.		

# LACTOSE, $C_{12}H_{22}O_{11} \cdot H_2O$ (monohydrate)

(Milk Sugar, Sugar of Milk, Lactobiose,

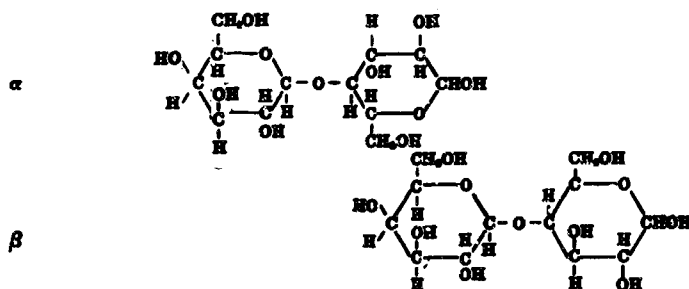
D-Glucose 4-( $\beta$ -D-galactoside),

D-Glucose 4-( $\beta$ -D-galactopuranside),

4-( $\beta$ -D-galactosyl)-D-glucose,

4-( $\beta$ -D-galactopyranosyl)-D-glucose)

Chemical Structure: Lactose consists of a glucose unit linked to a galactose unit. Because the glucose unit may be in the form of a lactol ring,  $\alpha$  and  $\beta$  forms are possible. The two forms can be represented as follows:



The second formula differs from the first only in that the second glucose ring has been turned through an angle of  $180^\circ$ . The glucose rings may also have the aldehyde structure. Both forms show mutarotation  $[\alpha]_D^{20} = +52.3$ .

The usual form is the  $\alpha$ . By crystallizing solutions of the  $\alpha$  form above  $93.5^\circ\text{C}$ , the  $\beta$  form is obtained.

Specification No.: MIL-L-13751

Molecular Weight: 360.31

Crystalline Form: rhombic

Color: colorless

Density, g./ml.: 1.525.

Coefficient of Thermal Expansion: —

Heat of Formation, cal./mole at  $298^\circ\text{K}$ :

$\alpha$ -lactose  $\cdot H_2O$  -592,900

$\beta$ -lactose -533,800

Free Energy of Formation, cal./mole at  $298^\circ\text{K}$ :

$\alpha$ -lactose  $\cdot H_2O$  -418,200

$\beta$ -lactose -373,700

Entropy, cal./deg./mole at  $298^\circ\text{K}$ :

$\alpha$ -lactose  $\cdot H_2O$  99.1

$\beta$ -lactose 92.3

Melting Point:  $274.7^\circ\text{K}$  ( $201.6^\circ\text{C}$ ) for the anhydrous material when rapidly heated. The monohydrate when heated loses water and becomes anhydrous at  $120^\circ\text{C}$ .

Refs.

Addnl. Ref. 1

1

1

1

Addnl. Ref. 2

Addnl. Ref. 2

Addnl. Ref. 2

1, 29

**Lactose (page 2)**

**Heat of Fusion:**

**Boiling Point:**

decomposes

**Transition Point:**

366.6°K (93.5°C)

Addnl. Ref. 3

**Heat of Transition, cal./g.:**

$\alpha$ -anhydride to  $\beta$ , + 1.0

Addnl. Ref. 3

**Heat of Combustion, anhydrous, Kg.cal./mole (H<sub>2</sub>O liquid) at 20° and 1 atm.:**

1350.8

1

**MCLAL HEAT CAPACITY**

T, °K	C <sub>p</sub> , cal. K°	T, °K	C <sub>p</sub> , cal. K°	T, °K	C <sub>p</sub> , cal. K°
<b><math>\alpha</math>-LACTOSE MONOHYDRATE</b>					
(wt. of sample in vacuo, 88.517 g.)					
61.33	21.98	148.30	54.86	239.02	85.49
65.15	23.63	156.90	57.62	246.02	87.94
69.70	25.49	164.04	59.95	252.92	90.65
75.00	27.71	171.85	62.61	257.99	92.06
81.74	30.37	180.61	65.50	261.72	93.30
86.85	32.48	187.39	68.53	268.21	96.65
91.73	34.64	195.39	70.63	274.33	97.14
96.55	36.12	204.15	73.70	279.56	99.26
103.74	38.63	212.01	76.21	284.21	100.74
109.42	40.61	214.48	77.22	289.17	102.57
115.57	42.97	219.77	79.07	292.91	103.59
122.23	45.58	222.39	79.93	293.35	104.10
129.51	48.12	227.86	81.62	297.42	105.06
140.75	52.11	231.69	82.65		
<b><math>\beta</math>-LACTOSE</b>					
(wt. of sample in vacuo, 113.11 g.)					
65.51	22.14	138.72	47.70	217.62	73.62
72.89	25.03	149.22	50.86	225.97	75.81
78.88	27.29	157.75	53.80	235.29	78.62
87.84	30.58	164.86	56.28	243.97	81.35
95.54	33.19	173.35	58.90	252.86	84.53
104.51	36.22	183.05	61.23	262.76	86.95
114.32	39.58	190.47	63.68	270.93	89.60
121.77	42.02	201.24	67.43	280.11	92.39
129.98	44.61	208.73	69.97	289.44	95.56

**Decomposition Temperature:**

**Decomposition Products:**

**Vapor Pressure:**

decomposes

**X-Ray Crystallographic Data:**

monoclinic system

**Lactose (page 3)****Hygroscopicity:**

Equilibrium Relative Humidity, % at 25°C: 98.3

Addnl. Ref. 5

**Solubility Data:** In cold water:

17 g./100 ml.:

1

In hot water:

40 g./100 ml.:

In alcohol:

very slightly soluble

In chloroform and ether:

insoluble

**SOLUBILITY IN WATER**

Addnl. Ref. 4

Temp. °C	Initial Solubility		Final Solubility	Super Solubility
	$\alpha$	$\beta$		
0	5.0	45.1	11.9	25
25	12.6	—	21.6	50
39	—	—	31.5	74
74	34.4	—	83.2	
89	55.7	—	139.2	
100	—	94.7	—	

**Health Hazard:**

nontoxic

used in infant feeding

29, 93

**Safety Classifications:**

OSM:

not listed

ICC:

not listed

**Fire and Explosion Hazard (dust ignited electrically in the presence of air):**

86

Concn. mg./l.	Max. Press. lbs./sq. in.	Ave. Rate of Press. Rise lbs./sq. in./sec.	Max. Rate of Press. Rise lbs./sq. in./sec.
100	12	89	177
500	22	32	168

**Electrostatic Sensitivity:**

—

**Apparent Dissociation Constants:**

Addnl. Ref. 4

First constant, literature values:

 $0.76-1.05 \times 10^{-12}$ 

Second constant, literature values:

 $3.0-3.6 \times 10^{-14}$ 

Third constant:

 $1.7 \times 10^{-14}$ 

Fourth constant:

 $1.6 \times 10^{-14}$ **Use in Pyrotechnics:**fuel, retardant, and in  
smoke mixtures

**Lactose (page 4)**

**Additional References:**

- 1) "Organic Chemistry," G. Hill and L. Kelley, The Blakiston Company, Philadelphia, Pa. (1943)
- 2) "Heat Capacities of Three Disaccharides," A. Anderson and G. Stegman, J. Am. Chem. Soc. *63*, 2113 (1941)
- 3) J. Am. Chem. Soc. *50*, 960-967 (1928)
- 4) "Lactose and Its Utilization, A Review," E. O. Whittier, J. Dairy Science, *27*, 505 (1944)
- 5) C.A. *51*, 17846 (1957)



## LAMINAC 4116

Refs.

Laminac 4116, a proprietary product manufactured by American Cyanamid Co., is a polyester with monomeric styrene that effects cross linking on curing. It is used as a bonding agent and for this purpose it is treated with a catalyst to effect curing.

The following data are from the technical data sheet on Laminac Polyester Resins of the Plastics and Resins Division of American Cyanamid Co.

Color:	clear, light straw
Specific Gravity at 77°F:	1.10 ± 0.02
Viscosity at 77°F:	
Gardner Holdt scale	M-0
Brookfield, poises	4-5
(Brookfield Model RVF, spindle #1, 20 R.P.M.)	

### Curing Characteristics:

Gelttime at 80°C, 100 g. sample, 0.5% benzoyl peroxide, min.:	17-20
SPI gel time, min.:	4½-8
SPI time to peak temp., min.:	7½-9
SPI peak exotherm, °F:	330-360
(SPI = Society of Plastic Industries Test Method)	

The curing of Laminac 4116 is greatly speeded by adding curing agents. The curing is done either at room temperature or by heating. Room temperature curing agents are methylethylketone peroxide and cobalt naphthenate, or benzoyl peroxide and Laminac Promoter 400.

### GEL TIMES AT 77°F (Methylethylketone peroxide (60% solution) as the catalyst)

% catalyst	% Cobalt Naphthenate 6% Cobalt metal	Gel time (minutes)
0.5	0.0	200-220
0.5	0.2	130-150
1.0	0.1	50-70
2.0	0.0	40-50
2.0	0.2	10-15

### GEL TIMES AT 77°F (Benzoyl peroxide (50% paste) as the catalyst)

% catalyst	% Cobalt Naphthenate 6% Cobalt metal	Gel time (minutes)
1.0	1.0	120-180
2.0	2.0	50-70
4.0	4.0	5-10

**Laminac 4116 (page 2)**

**Heat Cure:** Because of the low reactivity of Laminac 4116, its cure may not be complete with room temperature catalysts, and heat may be required to complete the cure. Benzoyl peroxide alone may be used to cure 4116 at elevated temperatures. Using 0.5-1.0%, cure cycles may be less than 1 minute at 260°F for a section 1/16 in. thick to 10-12 minutes for thicker sections at 200°F.

**Safety Classifications:**

OSM: class 2  
ICC: flammable liquid red label

**Decomposition Temperature:** about 200°C  
For TGA see Addnl. Ref. 5

**Decomposition Products:** —

**Hygroscopicity** (gain in mg./g. after exposure, at R.T. in static and vacuum desiccators):

Laminac 4116 Catalyzed with Lupersol DDM and Nuodex:

Time (days)	65% R.F.		75% R.H.		86% R.H.		93% R.H.	
	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.
1	3.0	1.5	5.2	3.5	6.5	<.1	3.5	3.0
7	5.0	2.5	3.7	4.0	4.7		7.2	2.5
30			0.3		1.0	2.0	1.6	

**Storage life of Laminac Resins with and without Catalyst and Accelerator:**

Temp. °C	Uncatalyzed (minimum)	With cobalt, but uncatalyzed (minimum)	With 0.004% cobalt and 0.5% Lupersol DDM
	days	days	hours
25	90	90	3.5-4.0
52	18-21	18-21	

As manufactured, Laminac resin contains 0.04% cobalt, as metal.

**Additional References:**

- 1) "Casting with Laminac Resins," Plastics and Resins Div., American Cyanamid Co., Wallingford, Conn., cited by Ref. 73
- 2) For exotherm cures of Laminac 4116 with varying amounts of Lupersol DDM and cobalt see Ref. 73
- 3) "The Kinetics of Thermal Degradation of the Synthetic Styrenated Polyester, Laminac 4116," D. Anderson and E. Freeman, J. Appl. Polymer Sc. 1, 192 (1959)
- 4) "Characterization of Saturated Polyesters by Differential Thermal Analysis," D. Anderson and E. Freeman, Anal. Chem. 31, 1697 (1959)
- 5) "Pre-ignition and Ignition Reactions of the Propagatively Reacting System Magnesium-Sodium Nitrate-Laminac," V. Hogan and E. Gordon, Combustion and Flame 3, No. 1, 3-12 (1959)

**LEAD CHROMATE,  $\text{PbCrO}_4$**   
(Pale Chrome, Permanent Yellow, and Paris, Leipzig,  
King's, Cologne, or Lemon Yellow Chrome)

Percent Oxygen:	19.80						
Specification No.:	JAN-L-488						
Molecular Weight:	323.22	1					
Crystalline Form:	monoclinic	1					
Color:	yellow or orange-yellow powder						
See also Ref. 54V11		1					
Density, g./ml.:	(solid) 6.8	1					
Coefficient of Thermal Expansion:	—						
Heat of Formation, Kcal./mole at 298°K:	(c) -217.7	9					
Free Energy of Formation, Kcal./mole at 298°K:	-203.6	86					
Entropy, cal./deg./mole at 298°K:	36.5	86					
Melting Point:	1117°K (844°C)	1					
Heat of Fusion:	not available	7					
Boiling Point:	decomposes above its melting point and gives off oxygen	1, 54V11					
Transition Point, °K:	(c) III $\xrightarrow{980}$ (c) II $\xrightarrow{1056}$ (c) I	9					
Heat of Sublimation:	—						
Heat Content or Enthalpy:	—						
Heat Capacity, cal./deg./mole (between 292 and 323°K):	(est.) (solid) 29.1	4					
Decomposition Temperature, °C:	approx. 904	45					
For DTA see Ref. 33							
Decomposition Products: Becomes reddish-brown at 250°C. At high temperatures it fuses and finally evolves oxygen with the formation of Cr <sub>2</sub> O <sub>3</sub> and basic lead chromate.		52V3					
Vapor Pressure:	—						
X-Ray Crystallographic Data:							
System	Space Group	<i>a</i>	<i>b</i>	<i>c</i>	Axial Angle	Molecules/ Unit Cell	
monoclinic	C <sub>2h</sub>	6.82	7.48	7.16	β = 102°33'	4	1

**Lead Chromate,  $PbCrO_4$  (page 2)**

**Hygroscopicity** (specification grade material, after 216 hrs. at 90°F):

R.H., %	55	70	90
Gain, %	0.01	0.02	0.09

33

**Solubility Data.** In water at 25°C: .0000058  
In acids and alkali hydroxides: soluble  
In acetic acid, ammonia: insoluble  
In hot water: insoluble

1, 29

**Health Hazard:** Partakes of the poisonous nature of both lead and chromium salts. Corrosive action on the skin, produces ulcers, and is associated with the formation of cancers. Produces anemia. Because of its low solubility, its toxicity is less than most other lead salts.

12

M.A.C., mg./m.<sup>3</sup> 0.1

14

**Safety Classifications:**

OSM: Class 2, when not packed or stored in original shipping container.

**Fire and Explosion Hazard:** Moderate by chemical reaction with reducing agents. Dangerous when heated, as it emits highly toxic fumes of lead.

12

**Electrostatic Sensitivity:** —

**Use in Pyrotechnics:** As an oxidizing agent. Used in nongaseous powders.

## LEAD OXIDE, PbO

(Litharge, Massicot, Plumbous Oxide, Lead Protoxide,  
Lead Monoxide, Lead Oxide Yellow)

Refs.

1, 29

Massicot refers to the unfused oxide and litharge, to the fused. Modern usage tends to the use of litharge for all varieties of PbO.

Specification No. (litharge, dry): MIL-L-1147  
Molecular Weight: 223.21  
Crystalline Form (litharge): tetragonal—stable  
at R.T.

(massicot): rhombic—stable,  
300°C to M.P.

22

Color: yellow

For the effect of temp. See Ref. 52V7

Density, g./ml.: (solid)  $\alpha$  litharge, 9.63  
 $\beta$  massicot, 8.0

1

Coefficient of Thermal Expansion, cubic:  $7.95 \times 10^{-6}$

54V7

Heat of Formation, Kcal./mole, at 298°K: red (c) -52.40  
yellow (c) -52.07

8, 9

See Tables a, b, c

Free Energy of Formation, Kcal./mole at 298°K: red (c) -45.25  
yellow (c) -45.05

1, 8, 9

See Tables a, b, c, and equations

### a. HEAT AND FREE ENERGY OF FORMATION OF PbO (red, yellow)

2

T, °K	$\Delta H$ (cal./mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . .	-52,450 ( $\pm 400$ )	-45,250 ( $\pm 150$ )
400 . . . . .	-52,250	-42,850
500 . . . . .	-52,050	-40,500
600 . . . . .	-51,800	-38,200
600.5 . . . .	-51,800	-38,200
600.5 . . . .	-53,050	-38,200
700 . . . . .	-52,800	-35,750
762 . . . . .	-52,600	-34,250
762 . . . . .	-52,350	-34,250

Phase Changes of Metal

M.P., 600.5°K;  $\Delta H = 1225$  cal./g.-atom

## Lead Oxide, PbO (page 2)

b. HEAT AND FREE ENERGY OF FORMATION OF  
PbO (yellow, l, g)

2

T, °K	$\Delta H$ (cal./mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . .	-52,050 ( $\pm 300$ )	-45,050 ( $\pm 150$ )
400 . . . . .	-51,900	-42,700
500 . . . . .	-51,750	-40,400
600 . . . . .	-51,550	-38,150
600.5 . . . .	-51,550	-38,150
600.5 . . . .	-52,800	-38,150
700 . . . . .	-52,500	-35,750
800 . . . . .	-52,200	-33,350
900 . . . . .	-51,850	-31,000
1000 . . . . .	-51,450	-28,750
1100 . . . . .	-51,000	-26,450
1159 . . . . .	-50,700	-25,150
1159 . . . . .	-47,900	-25,150
1200 . . . . .	-47,700	-24,400
1300 . . . . .	-47,250	-22,450
1400 . . . . .	-46,750	-20,550
1500 . . . . .	-46,250	-18,700
1600 . . . . .	-45,750	-16,850
1700 . . . . .	-45,300	-15,100
1745 . . . . .	-45,100	-14,300
1745 . . . . .	+5,700	-14,300

Phase Changes of Metal  
M.P., 600.5°K;  $\Delta H = 1225$  cal./g.-atom

## c. HEAT AND FREE ENERGY OF FORMATION OF PbO(g)

2

T, °K	$\Delta H$ (cal./mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . .	+10,100 ( $\pm 1400$ )	+5000 ( $\pm 1500$ )
400 . . . . .	+9900	+3200
500 . . . . .	+9700	+1800
600 . . . . .	+9500	0
600.5 . . . .	+9500	0
600.5 . . . .	+8300	0
700 . . . . .	+8000	-1400
800 . . . . .	+7800	-2700
900 . . . . .	+7600	-4000
1000 . . . . .	+7400	-5300
1100 . . . . .	+7200	-6600
1200 . . . . .	+7000	-7800
1300 . . . . .	+6700	-9000
1400 . . . . .	+6500	-10,300
1500 . . . . .	+6300	-11,400
1600 . . . . .	+6000	-12,600
1700 . . . . .	+5800	-13,800
1800 . . . . .	+5600	-15,000
1900 . . . . .	+5300	-16,100
2000 . . . . .	+5100	-17,200

Phase Changes of Metal  
M.P., 600.5°K;  $\Delta H = 1225$  cal./g.-atom

Source of Data: Heat of formation at 1745°K derived from heat of formation and heat of vaporization of PbO (l) (see Table b)

# Lead Oxide, PbO (page 3)

## Free Energy Equations:

Reaction	Range of Validity, °K	
1) $\text{Pb (c)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{PbO (red)}$ $\Delta F_T^\circ = -52,800 - 2.76T \log T - .80 (10^{-3}T^2) - .10 (10^5T^{-1}) + 32.49T$	298.16-600.5	2
2) $\text{Pb (l)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{PbO (red)}$ $\Delta F_T^\circ = -53,780 - .51T \log T - 1.75 (10^{-3}T^2) - .10 (10^5T^{-1}) + 28.44T$	600.5-762	
3) $\text{Pb (c)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{PbO (yellow)}$ $\Delta F_T^\circ = -52,040 + .81T \log T - 2.00 (10^{-3}T^2) - .10 (10^5T^{-1}) + 22.13T$	298.16-600.5	
4) $\text{Pb (l)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{PbO (yellow)}$ $\Delta F_T^\circ = -53,200 + 3.06T \log T - 2.95 (10^{-3}T^2) - .10 (10^5T^{-1}) + 18.08T$	600.5-1159	
5) $\text{Pb (l)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{PbO (l)}$ $\Delta F_T^\circ = -53,980 - 12.94T \log T + .25 (10^{-3}T^2) - .10 (10^5T^{-1}) + 64.22T$	1159-1745	
6) $\text{Pb (c)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{Pb (c)} + \frac{1}{2} \text{O}_2 \text{ (g)}$ $\Delta F_T^\circ = +10,270 + 1.91T \log T + 1.08 (10^{-3}T^2) + .295 (10^5T^{-1}) - 23.21T$	298.16-600.5	
7) $\text{Pb (l)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{PbO (g)}$ $\Delta F_T^\circ = +9300 + 4.17T \log T + .13 (10^{-3}T^2) + 2.95 (10^5T^{-1}) - 27.29T$	600.5-2000	
Entropy, cal./deg./mole at 298°K: (red)	15.9	2
(yellow)	15.6	3
See Tables d, e, f; also Addnl. Ref. 2		
Melting Point:	1159°K (886°C)	2, 9
Heat of Fusion, cal./mole at 298°K:	2800	2, 9
Boiling Point:	1745°K (1472°C)	2, 3, 9
Heat of Vaporization, kcal./mole:	51	9
Transition Point (from red to yellow)	762°K (489°C)	9
Heat of Transition, cal./mole:	290	2
See also Addnl. Ref. 2		
Heat of Sublimation:	—	

## d. HEAT CONTENT AND ENTROPY OF PbO (yellow, l) (Base, crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	1150	3.32	1100	10,800	16.90
500	2340	5.97	1159 (c)	11,720	17.72
600	3600	8.26	1159 (l)	18,720	23.76
700	4920	10.30	1200	19,380	24.32
800	6310	12.15	1300	20,980	25.60
900	7760	13.86	1400	22,580	26.79
1000	9260	15.44	1500	24,180	27.89

### PbO (yellow)

Enthalpy:  $H_T - H_{298.15} = 9.05T + 3.20 \times 10^{-3}T^2 - 2923$  (0.2 percent; 298 - 1159°K)

Heat Capacity:  $C_p = 9.05 + 6.40 \times 10^{-3}T$ ;  $\Delta H_{1159}$  (fusion) = 7000

### PbO (l)

Enthalpy:  $H_T - H_{298.15} = 16.00T + 180$  (0.1 percent; 1159 - 1745°K)

Lead Oxide, PbO (page 4)

e. HEAT CONTENT AND ENTROPY OF PbO (red)  
(Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	1220	3.52	700 . . . . .	5060	10.65
500 . . . . .	2480	6.28	800 . . . . .	6420	12.46
600 . . . . .	3740	8.62	900 . . . . .	7820	14.11

PbO (red) :

Enthalpy:  $H_T - H_{298.15} = 10.60T + 2.00 \times 10^{-5}T^2 - 3338$  (0.1 percent; 298-900°K)

Heat Capacity:  $C_p = 10.60 + 4.00 \times 10^{-5}T$

f. HEAT CONTENT AND ENTROPY OF PbO (g)  
(Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	810	2.34	1000 . . . . .	5950	10.14
500 . . . . .	1635	4.13	1200 . . . . .	7710	11.75
600 . . . . .	2480	5.72	1400 . . . . .	9480	13.11
700 . . . . .	3340	7.04	1600 . . . . .	11,250	14.29
800 . . . . .	4205	8.20	1800 . . . . .	13,030	15.34
900 . . . . .	5075	9.22	2000 . . . . .	14,810	16.28

PbO (g) :

Enthalpy:  $H_T - H_{298.15} = 8.57T + 0.12 \times 10^{-5}T^2 + 0.79 \times 10^5T^{-1} - 2831$   
(0.2 percent; 298-2300°K)

Heat Capacity:  $C_p = 8.57 + 0.24 \times 10^{-5}T - 0.79 \times 10^5T^{-2}$

PbO (c) :

Heat Capacity:  $C_p = 12.70 + 7.80 \times 10^{-5}T$  (est.) (298-1000°K)

Pb<sub>3</sub>O<sub>4</sub>(c) :

Heat Capacity:  $C_p = 35.14$  (298°K)

Pb<sub>2</sub>O<sub>3</sub>(c) :

Heat Capacity:  $C_p = 25.74$  (298°K)

See also Addnl. Ref. 2

Heat Capacity, cal./deg./mole at 298°K :

(solid, yellow) 11.60  
(liquid) 16.00

4, 9

See also Addnl. Ref. 2

Decomposition Temperature and Products: At 300-450°C, in air, it is converted to Pb<sub>3</sub>O<sub>4</sub>, but at higher temperatures it is reconverted to PbO.

29, Addnl.  
Ref. 1,  
54V7

For DTA see Ref. 33



# Lead Oxide, PbO (page 5)

## Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	943	1085	1189	1265	1402	1472	890

## X-Ray Crystallographic Data:

System	Space Group	a	b	c	Molecules/Unit Cell
tetragonal (red)	D <sub>4h</sub> <sup>1</sup>	3.98	—	4.01	2
rhombic (yellow)	V <sub>h</sub> <sup>19</sup>	5.50	4.72	5.88	4

Hygroscopicity (Baker's reagent grade, after equilibrium was established in a vacuum desiccator, gain in mg./g. at R. T.) 32

R.H.%	31	43	65	75	93
Time of Exposure	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.
Gain mg./g.	1.3 2.6	1.2 3.9	4.7 3.8	5.1 6.6	7.4 7.5

Critical R.H. at 25°: 99.2%

Solubility Data: In water: .0017 g./100 g. at 20° 1  
In HNO<sub>3</sub>, alk. lead acetate, NH<sub>4</sub>Cl, CaCl<sub>2</sub>, SrCl<sub>2</sub>, and warm solutions of 29  
fixed alkali hydroxides: soluble  
In alcohol: insoluble 1

Health Hazard: More poisonous than metallic lead or most other lead compounds. Avoid breathing dust. Wear approved dust mask. Keep away from food or food products: 12, 29

M.A.C., mg./m.<sup>3</sup>: 0.2 25  
0.15 14

## Safety Classifications:

OSM: not listed  
ICC: no shipping label required

Fire and Explosion Hazard: Dangerous. When heated emits highly toxic fumes. 12

Electrostatic Sensitivity: —

Use in Pyrotechnics: —

## Additional References:

- 1) C.A. 52, 6998 (1958)
- 2) "Low Temperature Heat Capacities and Entropies at 298.15°K of Lead Sesquioxide and Red and Yellow Lead Monoxide," E. G. King, J. Am. Chem. Soc. 80, 2400 (1958)

**LEAD OXIDE (LEAD TETROXIDE),  $Pb_3O_4$**   
**(Minium, Red Lead, Mineral Orange, Mineral Red,**  
**Plumbo, Puce, Orthoplumbate, Paris or Saturn Red)**

Percent Oxygen:	9.33
Specification No.:	TT-R-191b
The specification covers red lead for use in paints. Type I is dry, and has three grades (85, 95, 97) indicating the minimum % content of $Pb_3O_4$ . Type II paste in oil, grade 97.	
Molecular Weight:	685.63
Crystalline Form:	scales or amorphous powder
Color:	red
When heated becomes redder, then violet and black; on cooling again regains its scarlet red color.	
Density, g./ml.:	(solid) 9.1
Varies from 8.32 to 9.16 according to method of preparation.	
Coefficient of Thermal Expansion:	—
Heat of Formation, Kcal./mole at 298°K:	-175.8
See table below	
Free Energy of Formation, Kcal./mole at 298°K:	-147.6
See table below	

*Refs.*  
1, 11, 29

1  
1  
54V7

1  
54V7

1, 8, 9

1, 8, 9

**HEAT AND FREE ENERGY OF FORMATION OF  $Pb_3O_4(c)$**

T, °K	$\Delta H$ (cal./mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . .	-175,500 ( $\pm 4000$ )	-147,500 ( $\pm 4500$ )
400 . . . . .	-175,500	-138,000
500 . . . . .	-175,000	-129,000
600 . . . . .	-174,500	-119,500
600.5 . . . .	-174,500	-119,500
600.5 . . . .	-178,000	-119,500
700 . . . . .	-177,500	-110,000
800 . . . . .	-176,500	-100,500
900 . . . . .	-175,000	-91,000
1000 . . . . .	-173,500	-81,500

**Phase Changes of Metals**

M.P., 600.5°K;  $\Delta H = 1225$  cal./g.-atom

**Free Energy Equations:**

Reaction	Range of Validity, °K
1) $3Pb(c) + 2O_2(g) = Pb_3O_4(c)$	298.16-600.5
$\Delta F^\circ = -174,920 + 8.82T \log T - 8.20 (10^4 T^2) - .40 (10^6 T^{-1}) + 72.78T$	
2) $3Pb(l) + 2O_2(g) = Pb_3O_4(c)$	600.5-1000
$\Delta F^\circ = -177,860 + 15.59T \log T - 11.05 (10^4 T^2) - .40 (10^6 T^{-1}) + 60.57T$	
Entropy, cal./deg./mole at 298°K:	50.5

2

3, 9, 24

**Lead Oxide, Pb<sub>2</sub>O<sub>3</sub> (page 2)**

Melting Point:

decomposes at about  
773°K (500°C)

1

See Decomposition Temperature

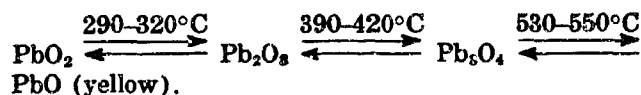
Heat of Fusion:

—

Boiling Point:

—

Transition Point:



Addnl. Ref. 2

Heat of Sublimation:

—

Heat Content or Enthalpy:

—

Heat Capacity, cal./deg./mole at 298°K:

(solid) 35.14

9

Decomposition Temperature and Products. Heated in air above 450°C, it is converted to PbO. About 550°.

Stable at 530°C.

For TGA see Ref. 45

29, Addnl.  
Ref. 1  
54V7

Vapor Pressure:

	for Pb <sub>2</sub> O <sub>3</sub>		PbO (yellow) + ½ O <sub>2</sub>				
Press. mm.	8.4	3.04	76.0	155	589	859	1045
Temp. °C	444.8	484.4	511.2	537.6	558.3	600.7	607

54V7

or  $\log_{10} p_{\text{mm.}} = 7.8595T^{-1} + 11.8976$

X-Ray Crystallographic Data:

System	Space Group	a	c	Molecules/Unit Cell
tetragonal	V <sub>4</sub>	8.875	6.51	4

18

Hygroscopicity (of reagent grade material after equilibrium was established in a vacuum desiccator):

22

R.H.%	65		75		86		93	
Time of Exposure	24 hrs.	equil.	24 hrs.	equil.	24 hrs.	equil.	24 hrs.	equil.
Gain, mg./g.	0.5	0.9*	0.2	0.1*	0.4	0.4*	0.8	0.6*

\*after one week

Solubility Data: In water and alcohol:  
In acetic acid, hot HCl

insoluble  
soluble

1

Health Hazard: A cumulative poison that produces anemia and lesions of the kidneys, liver, nervous system, blood vessels, and other tissues. The specification requires the following warning label: "Warning! Contains Lead Oxide Hazardous Dust. Avoid breathing dust and fumes. After handling or exposure do not eat or smoke without washing thoroughly. Use with adequate ventilation. Keep away from food or food products."

29, 14

M.A.C., mg./m.<sup>3</sup>:

0.2  
0.15

25  
14

**Lead Oxide, Pb<sub>2</sub>O<sub>3</sub> (page 3)**

**Safety Classifications:**

OSM:

class 2

ICC:

oxidizing material

yellow label

**Fire and Explosion Hazard:** Dangerous because when it is heated it emits highly toxic fumes. It reacts with combustible and reducing agents. 12

**Electrostatic Sensitivity:**

—

**Use in Pyrotechnics:**

as an oxidizer

17

**Additional References:**

- 1) C.A. 52, 6998 (1958)

LEAD PEROXIDE, PbO <sub>2</sub>			Refs.
(Lead Dioxide, Lead Superoxide, Brown Lead Oxide, Plattnerite)			1, 12, 29
Percent Oxygen:	13.3%		
Specification No.:	JAN-L-376		
Molecular Weight:	239.21		
Crystalline Form:	tetragonal		1
Color:	brown		
Density, g./ml.:	(solid) 9.375		Addl. Ref. 3
	(reguline at 20°C) 9.36		
Coefficient of Thermal Expansion, linear:	$0.057 \times 10^{-6}$		54V7
Heat of Formation, Kcal./mole at 298°K:	(c) -66.12		1, 9
See table below			
Free Energy of Formation, Kcal./mole at 298°K:	-52.34		1, 9
See table below			
HEAT AND FREE ENERGY OF FORMATION OF PbO <sub>2</sub> (c)			2
T, °K	Δ H (cal./mole)	Δ F° (cal./mole)	
298.16 . . . .	-66,100 (± 1400)	-52,300 (± 1200)	
400 . . . . .	-65,900	-47,700	
500 . . . . .	-65,700	-43,100	
600 . . . . .	-65,500	-38,600	
600.5 . . . .	-65,500	-38,600	
600.5 . . . .	-66,700	-38,600	
700 . . . . .	-66,400	-34,000	
800 . . . . .	-66,000	-29,400	
900 . . . . .	-65,500	-24,800	
1000 . . . . .	-65,000	-20,300	
1100 . . . . .	-64,400	-15,900	
Phase Changes of Metal			
M.P., 600.5°K; Δ H = 1225 cal./g.-atom			
Entropy, cal./deg./mole at 298°K:	18.3 ± 0.5		3, 9
Melting Point:	decomposes		1
Heat of Fusion:	—		
Boiling Point:	—		
Transition Point: See Lead Oxide (Lead Tetroxide), Pb <sub>3</sub> O <sub>4</sub>			
Heat of Sublimation:	—		
Heat Content or Enthalpy:	—		
Heat Capacity, cal./deg./mole at 298°K:	(solid) 15.4		9
Decomposition Temperature, °C:	290		1

**Lead Peroxide, PbO<sub>2</sub> (page 2)**

**Decomposition Products:** Evolves oxygen when heated above 300°C, first forming Pb<sub>2</sub>O<sub>4</sub>, and at high temperatures PbO.

17V8, 29  
Addnl.  
Ref. 5

**Vapor Pressure:**

Dissociation Pressure at 17°C atm.:  $7.1 \times 10^{-12}$

54V7

**X-Ray Crystallographic Data:**

System	Space Group	a	c	Molecules/Unit Cell
tetragonal	D <sub>4h</sub>	4.97	3.40	2

1

**Hygroscopicity** (reagent grade material after equilibrium was established in a vacuum desiccator at R.T.):

32

R.H., %	65		75		86		93	
Time of Exposure	24 hrs.	equil.	24 hrs.	equil.	24 hrs.	equil.	24 hrs.	equil.
Gain, mg./g.	0.3 0.1	0.2* 0.2	0.2 0.4	0.2* 0.6	0.1 0.5	.03	0.8 0.3	0.9 0.0

\*after one week

**Solubility:** In water and alcohol:

insoluble

In dil. HCl:

soluble

In acetic acid:

slightly soluble

1

**Health Hazard:** A cumulative poison. On ingestion or inhalation it produces anemia of the kidneys, liver, gonads, nervous system, blood vessels, and other tissues.

12, 17V8

**M.A.C., mg./m.<sup>3</sup>:**

0.2

25

0.15

14

**Safety Classifications:**

OSM: Class 2 when not packed or stored in original containers or equivalent.

ICC:

oxidizing material;  
yellow label

**Fire and Explosion Hazard:** Dangerous because when heated to decomposition it emits highly toxic fumes of lead. It reacts with reducing material.

12

**Electrostatic Sensitivity:**

---

**Changes under Heat and Oxygen Pressure:** Under 200 atmospheres of oxygen, PbO<sub>2</sub> is unstable to 360-365°C, but then dissociates to form Pb<sub>2</sub>O<sub>3</sub>, which is stable to 460-470°C when it passes into Pb<sub>2</sub>O<sub>4</sub>.

Addnl. Ref. 4

**Use in Pyrotechnics:**

as an oxidizer

17

**Additional References:**

- 1) "The Thermal Decomposition of Lead Dioxide in Air," G. Butler and J. Copp, J. Chem. Soc., 725 (1956)
- 2) "Structure and Equilibria of Lead Oxides," See C.A. 42, 6689 (1948)
- 3) "The Electrical Conductivity and Some Other Properties of Reguline Lead Peroxide," W. Palmaer, Z. Elektrochem 29, 415 (1923); C.A. 18, 616 (1924)
- 4) "A New Oxide of Lead," C. Holterman and P. Lafitte, Compt. rend., 204, 813 (1927); C.A. 31, 5702 (1937)
- 5) C.A. 52, 6998 (1958)

## LEAD SESQUIOXIDE

(Lead (III) Oxide, Lead (II, IV) Oxide, Lead Trioxide  
Plumbous Plumbate, Di-lead Trioxide)

Formula:	Pb <sub>2</sub> O <sub>3</sub>						
Pb <sub>2</sub> O <sub>3</sub> is generally considered to be lead metaplumbate (PbO·PbO <sub>2</sub> ) or a compound of PbO and PbO <sub>2</sub> into which it is decomposed by acids.		52V7					
Percent Oxygen:	10.38						
Specification No.:	none						
Molecular Weight:	462.42						
Crystalline Form:	monoclinic or amorphous powder	1					
Color:	yellow to reddish-yellow	1					
Density:	—						
Coefficient of Thermal Expansion:	—						
Heat of Formation:	—						
Free Energy of Formation:	—						
Entropy, cal./deg./mole at 298.15°K:	36.3 ± 0.7	Addnl. Ref. 1					
Melting Point:	decomposes about 643°K (370°C)	1					
Heat of Fusion:	—						
Boiling Point:	—						
Transition Point:	see Lead Oxide (Pb <sub>3</sub> O <sub>4</sub> )						
Heat of Sublimation:	—						
Heat Content or Enthalpy:	—						
Heat Capacity, cal./deg./mole at 298°K:	(solid) 25.74	4, Addnl. Ref. 1					
Decomposition Temperature: At 360–415°C it forms red lead with loss of O. At red heat yields PbO + O.		54V7					
Decomposition Products: Converted in air at 370°C to Pb <sub>3</sub> O <sub>4</sub> .		29					
Vapor Pressure:		—					
X-Ray Crystallographic Data:							
System	Space Group	a	b	c	Axial Angle	Molecules/Unit Cell	18
monoclinic	C <sub>2h</sub> <sup>2</sup>	7.050	5.616	3.865	β = 80°6'	2	
Hygroscopicity:		—					
Solubility Data: Insoluble in cold water, decomposes in hot. Decomposed by conc. HCl or H <sub>2</sub> SO <sub>4</sub> with the liberation of Cl or O respectively.		1					
		29					

**Lead Sesquioxide (page 2)**

**Health Hazard:** A cumulative poison when ingested, inhaled, or absorbed.

12

**M.A.C., mg./m.<sup>3</sup>:** 0.2

25

**Safety Classifications:**

**OSM:** Not listed. Probably class 2 when not packed or stored in original shipping container or equivalent.

**ICC:** not listed

**Fire and Explosion Hazard:** —

**Electrostatic Sensitivity:** —

**Use in Pyrotechnics:** as an oxidizing agent

**Additional References:**

- 1) "Low Temperature Heat Capacities and Entropies at 298.15°K of Lead Sesquioxide and Red and Yellow Lead Monoxide," E. G. King, J. Am. Chem. Soc. 80, 2400 (1958)



## LINSEED OIL

(Bung Oil, Bung Hole Oil, *Linum Usitatissimum*)

Linseed oil is obtained by pressing the seeds of the flax plant. The commercial oil is hot pressed. When fresh, the oil is yellowish with a peculiar odor and a bland taste; however, the hot pressed oil has a bitter taste. On exposure to the air, the oil slowly oxidizes, becoming darker, more viscous and acquires a stronger taste and odor. Boiled linseed oil is prepared by heating with metallic oxides, usually of lead or manganese (called driers). Such oil is called bung oil or bung hole oil. The state law of Ohio defines linseed oil as prepared pure linseed oil heated to a temperature of 225°F, incorporating not more than 4% by weight of drier, and with a specific gravity at 60°F of not less than 0.935 and not greater than 0.945. The oil dries in air with a glassy appearance and makes a hard yellowish film. The oxidized elastic solid is known as linoxyn.

Linseed oil is a mixture of glycerides of higher fatty acids, both saturated and unsaturated. Of these linoleic acid is about 48% and linolenic acid about 34%. Glycerides of stearic, palmitic, and myristic acids are also present. Addnl. Ref. 3 gives the following fatty acid analysis: 0.2 myristic, 5.4 palmitic, 3.5 stearic, 0.6 arachidic, 9.6 oleic, 42.6 linoleic, 38.1 linolenic.

Specification (for boiled linseed oil) :	TT-O-364	
(for raw linseed oil) :	TT-O-369	
Density, g./ml.:	0.930-0.938	1
Solidification Point, °C:	-19 to -27	1
Boiling Point:	616°K (343°C) 588.7°K (215.6°C) (600°F)	12 12 17
Decomposition Temperature and Products:	—	
Hygroscopicity:	nonhygroscopic	
Solubility Data:		
In alcohol:	slightly soluble	29
With chloroform, ether, petroleum ether, CS <sub>2</sub> , and oil of turpentine:	miscible	
Health Hazards: Slight. Boiled linseed oil contains a small amount of manganese dioxide. Because of this, if it is splashed in the eyes, it will cause extreme irritation. When handling keep linseed oil away from fire or open flame. Store it in a sealed container and away from oxidizing agents. If linseed oil has been splashed into the eyes, wash the eyes in a solution of one part vinegar and four parts water by volume. Send the victim to a physician for examination and additional treatment.		12
Safety Classifications:		
OSM: Not classified, but listed as a flammable liquid.		
ICC:	not listed	
Fire and Explosion Hazard: Flammable and can ignite spontaneously. To fight fire use foam, CO <sub>2</sub> , dry chemical, or CCl <sub>4</sub> .		26, 67, 75
Electrostatic Sensitivity:	—	

Refs.

16, 29, 57  
Addnl. Ref. 3

### Linseed Oil (page 2)

#### Constants for Linseed Oil (raw):

Maumené number:	103-126
Acid value:	1-3.5
Refractive index, $n_D^{25}$ :	1.4797-1.4802
Reichert-Meißl number:	0.95
Unsaponified matter:	0.4-1.2
Saponification value:	188-195
Iodine value:	175-202
Hehner's number:	94.5-95.5

#### Flash Point (closed cup) °F (literature references vary):

(raw)	from 401 to 468
(boiled)	from 378 to 403

#### Autoignition Temperature, °F:

Literature references give values ranging from 650 to 820.

#### Use in Pyrotechnics:

as a binder, a retardant,  
and to reduce  
hygroscopicity

#### Additional References:

- 1) "The Chemical Constitution of Natural Fats," T. P. Hilditch, London (1956)
- 2) "Vegetable Fats and Oils," E. W. Eckey, Reinhold Pub. Corp., New York (1954)
- 3) "Fats and Oils," H. G. Kinschenbauer, Reinhold Publishing Co., New York (1944)

1

12, 20

26, 67, 71

# LITHIUM, Li

Refs.

Specification No.:		
Molecular Weight:	6.940	
Crystalline Form:	cubic	1
Color:	silvery white, yellows on exposure to moist air	29
Density, g./ml.:	(solid) 0.534	1
Coefficient of Thermal Expansion, linear, 0-95°C:	$56 \times 10^{-6}$	27
	cubic, 0-178°C: $170 \times 10^{-6}$	
Heat of Formation, Kcal./mole at 298°K:	(gas) 37.07	1, 5
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 29.19	1, 5
Entropy, cal./deg./mole at 298°K:	(gas) 33.14	1, 5
See Tables a, b, and c		
Meiting Point:	726.8°K (453.70°C)	4, 5
Heat of Fusion, cal./mole:	722.8	5
Boiling Point:	1604°K ( 31°C)	5
Heat of Vaporization, cal./mole:	32,190	5
Transition Point:	(c) II → I 77°K (-196°C)	5, 41
Heat of Sublimation, cal./mole at 298°K:	(monatomic gas) 38,440	5
	(diatomic gas) 50,470	
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 1092	5
	(diatomic gas) 2312	
See Tables a, b, and c		
a. HEAT CONTENT AND ENTROPY OF Li (c, l)		4
(Base, crystals at 298.15°K)		

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350 . . . . .	315	0.97	900 . . . . .	4845	9.08
400 . . . . .	630	1.82	1000 . . . . .	5535	9.80
453.7 (c) . .	1000	2.68	1100 . . . . .	6225	10.46
453.7 (l) . .	1715	4.26	1200 . . . . .	6910	11.06
500 . . . . .	2050	4.96	1300 . . . . .	7595	11.61
600 . . . . .	2765	6.26	1400 . . . . .	8280	12.12
700 . . . . .	3465	7.34	1500 . . . . .	8960	12.58
800 . . . . .	4155	8.27	1600 . . . . .	9645	13.03

Li (c) :

Enthalpy:  $H_T - H_{298.15} = 1.64T + 5.55 \times 10^{-5}T^2 - 0.84 \times 10^{-6}T^3 - 701$  (0.1 percent; 298-453.7°K)

Heat Capacity:  $C_p = 1.64 + 11.10 \times 10^{-5}T + 0.84 \times 10^{-6}T^2$ ;  $\Delta H_{453.7}$  (fusion) = 715

Lithium, Li (page 2)

Li (l) :

Enthalpy:  $H_T - H_{298.15} = 6.78T - 0.99 \times 10^{-3}T^2 - 1143$  (0.1 percent; 453.7 - 1600°K)

Heat Capacity:  $C_p = 6.78 + 0.99 \times 10^{-3}T$

4

b. HEAT CONTENT AND ENTROPY OF Li (g)  
(Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	595	1.46	1900	7960	9.20
500	1005	2.57	2000	8460	9.46
600	1500	3.48	2200	9460	9.94
700	1995	4.24	2400	10,460	10.37
800	2495	4.90	2600	11,470	10.78
900	2990	5.49	2800	12,495	11.16
1000	3490	6.01	3000	13,525	11.51
1100	3985	6.49	3500	16,190	12.33
1200	4480	6.92	4000	19,010	13.08
1300	4980	7.32	4500	22,030	13.80
1400	5475	7.69	5000	25,315	14.49
1500	5975	8.03	6000	33,070	15.90
1600	6470	8.35	7000	43,240	17.46
1700	6965	8.65	8000	56,510	19.23
1800	7465	8.94			

Li (g) :

Enthalpy:  $H_T - H_{298.15} = 4.97T - 1482$  (0.2 percent; 298-3000°K)

c. HEAT CONTENT AND ENTROPY OF Li<sub>2</sub> (g) :  
(Base, ideal gas at 298.15°K; mol. wt., 13.88)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	390	2.59	1300	9115	13.30
500	1780	4.57	1400	10,050	14.00
600	2675	6.20	1500	10,985	14.64
700	3580	7.61	1600	11,925	15.25
800	4490	8.81	1700	12,865	15.82
900	5410	9.90	1800	13,815	16.36
1000	6330	10.87	1900	14,770	16.88
1100	7250	11.74	2000	15,725	17.37
1200	8180	12.55			

Lithium, Li (page 3)

Li<sub>2</sub> (g) :

Enthalpy:  $H_T - H_{298.15} = 8.93T + 0.16 \times 10^{-5}T^2 + 0.36 \times 10^{-8}T^3 - 2797$   
(0.1 percent; 298-2000°K)

Heat Capacity:  $C_p = 8.93 + 0.32 \times 10^{-5}T - 0.36 \times 10^{-8}T^2$

Heat Capacity, cal./deg./mole at 298°K: (solid) 5.91  
(gas, monatomic) 4.97  
(gas, diatomic) 8.62

d. HEAT CAPACITY OF Li

Solid	298-453.7°K
Liquid	453.7-1604°K
Gas (mon.)	1604-2000°K
T, °K	C <sub>p</sub> (cal./deg./mole)
298	5.91
400	6.50
500	7.20
600	7.06
900	6.90
1200	6.87
1600	6.80
1700	4.97
2000	4.96
2400	5.03
2800	5.13
3000	5.21

Decomposition Temperature: —

Decomposition Products: —

Vapor Pressure

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	723	881	1003	1097	1273	1372	186

X-Ray Crystallographic Data:

System	Space Group	a	Atoms/Unit Cell
cubic	O <sub>h</sub> <sup>1</sup>	3.502	2

Hygroscopicity: Reacts with water; forms LiOH, evolves H<sub>2</sub>.

Solubility Data: In water:

In alcohol:

In acids:

In liquid NH<sub>3</sub>:

forms LiOH, evolves H<sub>2</sub>

decomposes

soluble, reacts and  
evolves H<sub>2</sub>

soluble

Health Hazard: Will burn in contact with many substances, producing a caustic smoke which is toxic by inhalation. Dangerous when ingested or inhaled, and produces painful burns when in contact with the skin.

**Lithium, Li (page 4)**

**Safety Classifications:**

OSM: Not specifically listed; probably class 2 as a powdered metal.

ICC: flammable solid, yellow label

**Fire and Explosion Hazard:** Dangerous explosive hazard when exposed to heat, flame, or by chemical reaction with water, acids or oxidizers. On burning, it emits toxic fumes of  $\text{Li}_2\text{O}$  and  $\text{LiOH}$ . It burns in air with a dazzling bright light. Keep the metal submerged in kerosene. Store and process only in rooms or buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction with moisture. Suitable respiratory protective equipment and self-contained breathing apparatus should be used where permissible concentrations are likely to be exceeded. To fight fire, use special mixtures of dry chemicals, soda ash, or graphite. 14, 12, 16

**Autoignition Temperature, °F:** 392 12

**Electrostatic Sensitivity:** —

**Use in Pyrotechnics:** Burns with a brilliant crimson to carmine-red color. 1, 29

# LITHIUM NITRATE, $\text{LiNO}_3$

Refs.

Percent Oxygen:	69.62	
Specification No.:	—	
Molecular Weight:	68.95	
Crystalline Form:	trigonal	1
Color:	colorless	
Density, g./ml.:	(solid) 2.38	1
	(liquid) $d = 1.924 - .548 \times 10^{-4}t^\circ\text{C}$ (M.P. to $550^\circ\text{C}$ )	40V2
Coefficient of Thermal Expansion, at $254^\circ\text{C}$		
(molten) cubic:	about $3.15 \times 10^{-4}$	44V20
Heat of Formation, Kcal./mole at $298^\circ\text{K}$ :	(c) -115.28	1, 9
Free Energy of Formation, Kcal./mole at $298.16^\circ\text{K}$ :	-96.63	86
Entropy, cal./deg./mole at $298.16^\circ\text{K}$ :	38.4	86
See table below		
Melting Point:	$525^\circ\text{K}$ ( $252^\circ\text{C}$ )	4
Heat of Fusion, cal./mole:	6120	4
Boiling Point:	decomposes	
Transition Point:	—	
Heat of Sublimation:	—	

## HEAT CONTENT AND ENTROPY OF $\text{LiNO}_3$ (c, l) (Base, crystals at $298.15^\circ\text{K}$ )

4

T, $^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, $^\circ\text{K}$	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350 . . . . .	1130	3.50	525 (c) . . .	5380	13.29
400 . . . . .	2280	6.51	525 (l) . . .	11,500	24.95
450 . . . . .	3480	9.39	550 . . . . .	12,160	26.18
500 . . . . .	4730	12.03	600 . . . . .	13,490	28.49

### $\text{LiNO}_3$ (c) :

Enthalpy:  $H_T - H_{298.15} = 14.98T + 10.60 \times 10^{-5}T^2 - 5409$  (0.1 percent;  $298$ - $525^\circ\text{K}$ )

Heat Capacity:  $C_p = 14.98 + 21.20 \times 10^{-5}T$

### $\text{LiNO}_3$ (l) :

Enthalpy:  $H_T - H_{298.15} = 26.60T - 2470$  (0.1 percent;  $525$ - $600^\circ\text{K}$ )

Heat Capacity, cal./deg./mole: (liquid) 26.60

Decomposition Temperature and Products: When heated, gives off oxygen then a mixture of oxygen and nitrogen.

For DTA and TGA see Refs. 33, 47

Vapor Pressure

54V2

**Lithium Nitrate,  $\text{LiNO}_3$  (page 2)**

**X-Ray Crystallographic Data:**

System	Space Group	a	Axial Angle	Molecules/Unit Cell	
hexagonal	$D_{3h}^2$	5.74	$\alpha = 48^\circ 3'$	2	1

**Solubility:**

In water (g./100 ml.):	52 cold, 66 at $71^\circ\text{C}$	1
In acetic acid:	slightly soluble	

**Hygroscopicity:** Deliquescent. Caution: Keep in closed containers. 29

**Health Hazard:** Large amounts taken by mouth may be fatal. 12

**Safety Classifications:**

OSM: Class 1. Class 2 when not packed or stored in original shipping containers or equivalent.

ICC: oxidizing material

**Fire and Explosion Hazard:** A vigorous oxidizing agent. May explode when heated with a fuel, or when exposed to heat or by shock. On decomposition it emits toxic fumes.

**Electrostatic Sensitivity:**

Use in Pyrotechnics: as an oxidizer; to color burning compositions red 17



# LITHIUM PERCHLORATE, LiClO<sub>4</sub>

Refs.

Percent Oxygen:	60.15	
Specification No.:	none	
Molecular Weight:	106.40	
Crystalline Form:	no regular form recognizable	44V20
Color:	colorless	1
Density, g./ml.:	(solid) 2.429	1, 65
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	-91.77	72
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	509°K (236°C) 520°K (247°C)	9 Addnl. Ref. 1 65
Values vary from < 300 to 410°C, with decomposition.		
Boiling Point:	decomposes at 653°K (380°C)	1
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature, °C:	380	1
For DTA and TGA see Refs. 33, 47		
Decomposition Products:	LiCl + O <sub>2</sub>	29
Decomposition:	Does not begin to show an appreciable decomposition rate until the temperature is raised to over 400°C. There is an endothermic break at 610°C, corresponding closely to the melting point of LiCl (614°C). At about 420°C LiClO <sub>4</sub> begins to undergo appreciable loss. The temperature interval between salt fusion and onset of rapid decomposition is from 247 to about 502°C, or approximately a range of 255°C:	72 Addnl. Ref. 1
LiClO <sub>4</sub> · H <sub>2</sub> O loses H <sub>2</sub> O at 146°C		
The pure anhydrous salt can be heated to at least 300°C without decomposition, but ordinary samples decompose at lower temperatures to chloride and oxygen owing to the catalytic effect of dust and atmospheric impurities.		
Vapor Pressure:	—	Addnl. Ref. 1 52V7
X-Ray Crystallographic Data for LiClO <sub>4</sub> · 3H <sub>2</sub> O:		
System	Space Group	a c
hexagonal	C <sub>6v</sub>	7.71 5.42
Hygroscopicity:	deliquescent	1
Solubility Data: In water (g./100 g.):	59.7 at 25°C	1

**Lithium Perchlorate,  $\text{LiClO}_4$  (page 2)**

**Solubility in Nonaqueous Solvents at 25°C**

65, 72, 77

<i>Solvent</i>	<i>g./100 g. of Solvent</i>
acetone	136.5
ethyl acetate	95.2
ethyl ether	113.7
methyl alcohol	182
ethyl alcohol	151.8

**Health Hazard:** May irritate the skin and mucous membranes. Lithium salts are rated moderately toxic. They affect the nervous systems, and can cause death. 29, 65

**Safety Classifications:**

OSM: Class 1. Class 2 when not stored in original shipping containers or equivalent.

ICC: Oxidizing material; yellow label. Classed under "Explosives and Other Dangerous Articles."

**Fire and Explosion Hazard:** A powerful oxidizer, can cause fires by chemical reaction, and forms explosive mixtures with carbonaceous materials or finely divided metals, sulphur, powdered magnesium or aluminum. Explodes on shock or by chemical reaction. 12

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:**

as an oxidizer; to color  
burning compositions red

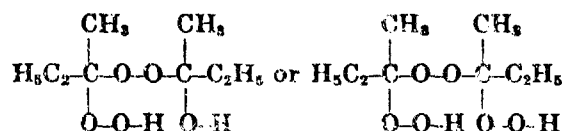
**Additional References:**

- 1) "The Differential Thermal Analysis of Perchlorates. II. The System  $\text{LiClO}_4 - \text{LiCO}_3$ ," M. M. Markowitz, J. Phys. Chem. 62, 827 (1958)
- 2) "Precise Studies of the Crystal Structures of Lithium Perchlorate Trihydrate, Anhydrous Lithium Perchlorate, and Potassium Perchlorate," R. J. Prosen and K. N. Trueblood, Perchlorates TN-2, CSR TN 56-563, ASTIA Document No. AD110-384 (1956)

## LUPERSOL DDM

Lupersol DDM is a proprietary mixture of 60% methylethylketone peroxide in dibutylphthalate, marketed by the Lucidol Div., Wallace and Tiernan, Inc., Buffalo, New York. The following data, except where otherwise indicated, are from the Lucidol Div., Wallace and Tiernan.

The structure of methylethylketone peroxide is:



The market product has about 11% active oxygen.

Stability: Lupersol loses about 7% of its peroxide content after 12 months of storage at ambient temperatures (20-80°F).

### DECOMPOSITION KINETICS

Active %	Conc. g. moles peroxide (-O-O-)/l.	Temp. °C	Half Life t ½ in hrs.	First Order Rate k./hr.	E (Activation Energy) Kcal./mole
11 at start	0.2	85	81.2	0.00854	
		100	16.2	0.0428	
		115	3.6	0.193	28.5
		145	0.25	2.77	

### DECOMPOSITION TEMPERATURES IN BENZENES AT SELECTED HALF LIFE VALUES

Time	1 min.	10 hrs.	100 hrs.
Temp. C°	182	105	83

Solubility Data: Soluble in most synthetic resin monomers.

Health Hazard: Highly toxic by ingestion.

Safety Classifications:

OSM: Not specifically listed but peroxides are in class 1 when stored in original shipping containers, and in class 2 when not in original shipping containers or the equivalent.

ICC: Not specifically listed, but organic peroxides not otherwise specified are classed as flammable liquids and as oxidizing materials under "Explosives and Other Dangerous Articles."

Fire and Explosion Hazard: Methylethylketone peroxide alone is shock sensitive. To reduce the sensitivity to shock, it is diluted with dibutylphthalate and is then acceptable for shipment. The peroxide may exist in several different structures, some of which are extremely shock sensitive even in 60% solution. The solution may thus be a hazard. Lupersol DDM will decompose rapidly at 125°C. The solution has a flash point (open cup) above 45°C and burns like gasoline when ignited. Lupersol DDM is widely used

Refs.

Addnl. Ref. 2

Addnl. Ref. 1

Addnl. Ref. 2

Addnl. Ref. 2

12

12, Addnl. Ref. 3

#### Lupersol DDM (page 2)

as a room temperature catalyst with cobalt naphthenate or similar metallic drier as the accelerator. Mixtures of the peroxide and accelerator will decompose explosively and the two should not be brought into direct contact. As a powerful oxidizing agent, the peroxide can react vigorously with reducing materials.

Storage Precautions: Store in an isolated building with no other type of material. Buildings containing the peroxide should be posted "Flammable Storage—Keep Fire Away."

Disposal of Lupersol DDM: Burning, the preferred method, or chemical hydrolysis.

Burning Method: Pour material to be destroyed into shallow trench. Ignite with a wadded gasoline soaked rag tied to the end of a 6-ft. steel rod. Boiling will be rapid but not violent.

Chemical Hydrolysis Method: Slowly add peroxide solution to 10 times its weight of 20% NaOH solution with constant stirring. The reaction is exothermic. Decomposition shall be complete in 24 hours, and is confirmed when an acidified sample of the alkaline reaction mixture does not liberate iodine from an acetone solution of NaI.

Electrostatic Sensitivity: — —

Use in Pyrotechnics: Usually with cobalt naphthenate (g.v.) to cure Laminac 4116 (see PA-PD-594).

Addnl Ref. 3

#### Additional References:

- 1) Chem. Eng. News (Dec. 7, 1959) (Wallace and Tiernan advertisement).
- 2) "The Evaluation of Organic Peroxides on the Basis of Half Life Data," D. Doehnert and O. Mageli, *Modern Plastics* 36, 142 (1959)
- 3) "The Use of Organic Peroxides," C. H. Rybolt, paper presented at the 11th meeting of The Reinforced Plastics Division, S.P.I., Atlantic City, New Jersey (1956)
- 4) For use with Laminac 4116, see Ref. 73

# MAGNESIUM, Mg

Refs.

Specification No.:

JAN-M-382

The specification covers three types. Types I and II must be manufactured by grinding, stamping, turning, or any combination of these methods which will yield a suitable product. Type II must be manufactured by the atomizing process. Type I is divided into two grades which differ in purity. Type I, grade A, and types II and III all have the same purity requirements. Grade B is ordinarily manufactured from scrap.

Molecular Weight:	24.32	
Crystalline Form:	hexagonal	1
Color:	silvery white	1
Density, g./ml.:	1.74	1
Coefficient of Thermal Expansion at 20-100°C:	$26 \times 10^{-6}$	1
Temp. °C	Coeff.	
-183 to +15	$21.40 \times 10^{-6}$	
20-200	$27.9 \times 10^{-6}$	
20-500	$29.8 \times 10^{-6}$	
Heat of Formation, Kcal./mole at 298°K:	(gas) -35.6	5
Free Energy of Formation, Kcal./mole at 298°K:	(gas) -27.341	5
Entropy, cal./deg./mole at 298°K:	(c) 7.31	5
	(gas) 35.51	5
See Tables a and b		
Melting Point:	923°K (650°C)	5, 7
Heat of Fusion, cal./mole:	2140	4, 5
Boiling Point:	1390°K (1117°C)	5
Heat of Vaporization, cal./mole:	30,750	5
Transition Point:	---	
Heat of Sublimation, cal./mole at 298°K:	35,600	5
Heat Content or Enthalpy, cal./mole at 298°K:	1195	5

## a. HEAT CONTENT AND ENTROPY OF Mg (c, l) (Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	615	1.78	923 (l)	6415	9.86
500	1255	3.20	1000	7020	10.48
600	1920	4.41	1100	7800	11.23
700	2610	5.48	1200	8580	11.91
800	3330	6.44	1300	9360	12.53
900	4095	7.34	1400	10,140	13.11
923 (c)	4275	7.54			

Mg (c):

Enthalpy:  $H_T - H_{298.15} = 4.97T + 1.52 \times 10^{-5}T^2 - 0.04 \times 10^{-5}T^3 - 1604$  (0.2 percent; 298-923°K)

Heat Capacity:  $C_p = 4.97 + 3.04 \times 10^{-5}T + 0.04 \times 10^{-5}T^2$

Magnesium, Mg (page 2)

Mg (l) :

Enthalpy:  $H_T - H_{298.15} = 7.80T - 780$  (0.1 percent; 923-1400°K)

b. HEAT CONTENT AND ENTROPY OF Mg (gas)  
(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	505	1.46	1900	7960	9.20
500	1005	2.57	2000	8455	9.46
600	1500	3.46	2200	9450	9.93
700	1997	4.24	2400	10,445	10.36
800	2495	4.90	2600	11,440	10.76
900	2990	5.49	2800	12,440	11.13
1000	3490	6.01	3000	13,440	11.48
1100	3985	6.49	3500	15,980	12.26
1200	4480	6.92	4000	18,610	12.96
1300	4980	7.32	4500	21,400	13.62
1400	5475	7.69	5000	24,410	14.25
1500	5970	8.03	6000	31,355	15.52
1600	6470	8.35	7000	39,955	16.84
1700	6965	8.65	8000	50,805	18.28
1800	7465	8.93			

Mg (g) :

Enthalpy:  $H_T - H_{298.15} = 4.97T - 1482$  (0.2 percent; 298-3500°K)

4

Heat Capacity, cal./deg./mole at 298°K: (solid) 5.96  
(liquid) 7.80  
(gas) 4.97

4, 5

c. HEAT CAPACITY OF Mg

5

Solid 298-923°K	
Liquid 923-1390°K	
Gas (mon) 1390-3000°K	
T, °K	$C_p^\circ$ (cal./deg./mole)
298	5.96
400	6.24
600	6.76
800	7.42
900	7.81
1000	7.88
1100	8.14
1200	8.40
1300	8.66
1400 to	
2400	4.97
2500	4.98
3000	5.02

Magnesium, Mg (page 3)

Decomposition Temperature and Products:

For TGA see Addnl. Ref. 7

For TGA and DTA see also Ref. 33

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	621	743	838	909	1034	1107	651

X-Ray Crystallographic Data:

System	Space Group	a	c	Atoms/Unit Cell
hexagonal	D <sub>6h</sub> <sup>4</sup>	3.203	5.196	2

Hygroscopicity:

slowly oxidizes in moist air

Grade B material (see Spec. grades)	R.H. at 70°F	Time of Exposure, hrs.	Gain in weight, %
	50	216	0.06
	70	216	0.22
	90	168	0.62

Solubility Data: Insoluble in cold water; slightly soluble in hot; decomposing to Mg (OH)<sub>2</sub>. Soluble in mineral acids (except CrO<sub>3</sub>), conc. HF, NH<sub>4</sub> salts. Insoluble in alkalis. Reacts readily with dilute acids with evolution of hydrogen.

Health Hazard: Slightly to moderately toxic. Particles which perforate the skin may produce severe local tumors characterized by the formation of pockets of gas and acute inflammatory reaction, frequently with necrosis (chemical gas gangrene). Inhalation of fumes or dust may irritate the respiratory tract.

M.A.C.: 10 pts. per million in air and 15 mg./m.<sup>3</sup> of fumes as MgO.

Safety Classifications:

OSM: Class 1; class 2 when not stored in original shipping containers or equivalent.

ICC: Magnesium scrap (shavings, borings or turnings) is classed as a flammable solid; yellow label.

Fire and Explosion Hazard: Contact with water may cause ignition of powdered magnesium evolution of hydrogen, and explosion. Dangerous in the form of dust or flakes when exposed to flame or by chemical action with an oxidizing agent. Finely divided magnesium can be ignited by a spark or match flame. Highly explosive. Caution: water, CO<sub>2</sub>, or carbon tetrachloride should not be used on magnesium fires. Use G-1 powder or powdered talc on open fires and boron trichloride on oven fires.

Store and process only in rooms or buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction of powdered metal and moisture. In the repair and maintenance of buildings or equipment, powder or dust should be removed and non-sparking tools used.

**Magnesium, Mg (page 1)**

Electrostatic Sensitivity: Minimum energy required for ignition of powder by electric sparks (millijoules):

Type	Dust Layer	Cloud Layer	
atomized	120	40	26, 51
milled	40	8	
stamped	20	1	

Can be ignited by a spark in an atmosphere of CO<sub>2</sub> or in air-nitrogen mixtures with not less than 3% oxygen. To avoid ignition process in helium. 49, 51

Ignition Temperatures of Magnesium Powders, °C: 26, 50

Type	Dust Cloud	Dust Layer
atomized	600	490
milled	540	475
stamped	520	480

Minimum Explosive Concentration, mg./l.: (atomized) 10 26, 50  
(milled) 20  
(stamped) 20

Use in Pyrotechnics: As a fuel, and in tracer, igniter, signal flare, and pyrotechnic compositions.

**Additional References:**

- 1) "The Kinetics of Underwater Corrosion of Powdered Magnesium," E. Freeman and S. Gordon, *J. Phys. Chem.* 50, 1009 (1955)
- 2) "Magnesium and Its Alloys," C. S. Roberts, John Wiley & Sons, New York (1960)
- 3) "National Fire Codes, vol. 11, The Prevention of Dust Explosions," National Fire Protection Association, Boston, Mass. (1952)
- 4) "Safety Requirements for Manufacturing and Processing Military Pyrotechnics," ORDM 7-255 (1952)
- 5) *C. A.* 37, 2578 (1943)
- 6) Ref. 64
- 7) *Combustion and Flame* 3, No. 1, 3-12 (1959)



# MAGNESIUM-ALUMINUM ALLOY (MagnaIium)

Refs.

Specification No.:	JAN-M-454											
The specification covers two types, A and B, which differ in granulation (B is coarser): A - 56/50 Mg/Al, approx. 53.3 atom % Mg. B - 35/35 Mg/Al, approx. 67.0 atom % Mg.		Spec.										
Molecular Weight:	-----											
Color and Form:	silvery metal											
Density, g./ml.:	(solid) type A, about 2.142 type B, about 2.015											
Calculated on the basis of data in Addnl. Ref. 3												
Coefficient of Thermal Expansion:	type A, approx. $29.3 \times 10^{-6}$ type B, approx. $28.7 \times 10^{-6}$											
By interpolation from Addnl. Ref. 2												
Heat of Formation, cal./mole at 298°K:	type A, -1027	24										
Boiling Point: Decreases with increasing Mg content.		44S35										
<table><tr><td>Wt. % Mg</td><td>20</td><td>40</td><td>60</td><td>80</td></tr><tr><td>B.P. °C</td><td>1300</td><td>1200</td><td>1150</td><td>1115</td></tr></table>			Wt. % Mg	20	40	60	80	B.P. °C	1300	1200	1150	1115
Wt. % Mg	20	40	60	80								
B.P. °C	1300	1200	1150	1115								
Vapor Pressure: See Addnl. Refs. 2 and 4												
X-Ray Crystallographic Data:												
<table><tr><td></td><td>a</td><td>Atoms/Unit Cell</td></tr><tr><td>type A</td><td>about 10.46</td><td>about 58</td></tr><tr><td>type B</td><td>about 10.57</td><td>about 58</td></tr></table>				a	Atoms/Unit Cell	type A	about 10.46	about 58	type B	about 10.57	about 58	
	a	Atoms/Unit Cell										
type A	about 10.46	about 58										
type B	about 10.57	about 58										
By interpolation and extrapolation of data in Addnl. Ref. 3												
Hygroscopicity: Cumulative increase in weight after storage:												
over water for 29 days 6.3%	over H <sub>2</sub> SO <sub>4</sub> for 29 days 4.7%	2 days in oven at 105°C 4.3%										
Solubility Data:	see Magnesium and Aluminum	51										
Health Hazard:	no known toxicity	50V8										
Safety Classifications:												
OSM: No classification given. Since Al and Mg powders are in class 1, powdered Mg/Al alloy is probably similarly classified.												
ICC: No classification given. However, since powdered metallic magnesium is classified under "Explosives and Other Dangerous Articles," the alloy would be similarly classified as a flammable solid requiring a yellow label.												
Fire and Explosion Hazard: Prevent water from contacting the powdered material. Store and process only in rooms or buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction of powdered metal and moisture. Powdered Mg/Al alloy mixed with oxidizing agents is a dangerous fire and explosion hazard. Powdered metal exposed to the air is a dangerous fire hazard, and when ignited burns with intense heat. In the repair or maintenance of buildings or equipment, powder or dust should be removed and nonsparking tools used.												
Minimum Explosive Concentration of type A Mg/Al powder is 50 mg./l.												

**Magnesium-Aluminum (magnalium) (page 2)**

Electrostatic Sensitivity: Minimum energy required for ignition of powder by electric sparks, millijoules:	(dust cloud) 80 (dust layer) 20	26, 50
Ignition Temperature, °C of type A alloy:	(dust cloud) 535 (dust layer) 46	26, 50
Use in Pyrotechnics:	as fuels	

**Additional References:**

- 1) "Magnesium and Its Alloys," by C. S. Roberts, John Wiley & Sons, New York (1960)
- 2) "The Physical Metallurgy of Magnesium and its Alloys," G. V. Raynor, Pergamon Press, New York (1959). Contains a good phase diagram of the system Mg/Al, plus a discussion.
- 3) "Handbook of Lattice Spacings and Structures of Metals," W. B. Pearson, Pergamon Press, New York (1958)
- 4) A. Schneider and E. K. Stoll, Z. Electrochem. 47, 519 (1941)

# MAGNESIUM CARBONATE, $\text{MgCO}_3$

		Refs.
Specification No.:	MIL-M-11361	
Molecular Weight:	84.33	
Crystalline Form:	trigonal	1
Color:	white	1
Density, g./ml.:	(solid) 3.037	1
Coefficient of Thermal Expansion, cubical:	$0.5 \times 10^{-7}$	31
Heat of Formation, Kcal./mole at 298°K:	-266	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	-246	1, 9
Entropy, cal./deg./mole at 298°K:	15.7	1, 9
See table below		
Melting Point:	decomposes at 623°K (350°C)	1
Heat of Fusion:	—	
Boiling Point:	loses $\text{CO}_2$ at 1173°K (900°C)	1
Transition Point:	—	
Heat of Sublimation:	—	

## HEAT CONTENT AND ENTROPY OF $\text{MgCO}_3$ (c) (Base, crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	2060	5.92	700 . . . . .	9450	19.54
500 . . . . .	4300	10.91	750 . . . . .	10,820	21.43
600 . . . . .	6790	15.45			

$\text{MgCO}_3$ (c):		
Enthalpy: $H_T - H_{298.15} = 18.62 + 6.90 \times 10^{-5}T^2 + 4.16 \times 10^{-8}T^3 - 7560$		
(0.4 percent; 298-750°K)		
Heat Capacity: $C_p = 18.62 + 13.80 \times 10^{-5}T - 4.16 \times 10^{-8}T^2$		
Heat Capacity, cal./deg./mole:	(solid) 18.05	9
Decomposition Temperature:	900°C	64
For TGA see Addnl. Ref. 1		
Magnesite (mineral $\text{MgCO}_3$ ) begins to lose $\text{CO}_2$ at 450-500°C		50V5
Decomposition Products:	$\text{MgO} + \text{CO}_2$	29
Vapor Pressure:		42V7

Press. atm.	.0001	.0089	.0776	0.983	1.763	13.87	473.4
Temp. °K	673.1	723.1	763.1	813.1	843.1*	873.1*	973.1*

\*calculated from equation

$$\log kp_1 - \log kp_2 = \frac{\Delta H (T - T_2)}{4.571 (T \cdot T_2)}, \Delta H = 60.863$$

**Magnesium Carbonate,  $MgCO_3$  (page 2)**

**X-Ray Crystallographic Data:**

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell</i>	
hexagonal	$D_{6h}^2$	5.61	$\alpha = 120^\circ$	2	1
Hygroscopicity:					
Solubility Data: In water:			.0106 g./100 ml.		1, 29
More soluble in water containing $CO_2$ .					
In acids:			soluble, reacts with evolution of $CO_2$		
In acetone, $NH_3$ , and alcohol:			insoluble		
Health Hazard: None. Has an antacid and laxative effect. Slight to moderate on ingestion and inhalation.					29, 93
Safety Classifications:					_____
Fire and Explosion Hazard:					_____
Electrostatic Sensitivity:					_____
Use in Pyrotechnics:			as a retardant		
Additional References:					
1) J. Am. Ceram. Soc. 33, 96-101 (1950)					

# MAGNESIUM OXIDE, $MgO$

(Magnesia, Calcined Magnesia, Dead Burned Magnesia, Light Magnesia, Ponderosa Magnesia, Magnesia Usan Periclase)

Specification No.:	MIL-M-12836A	
The spec. covers one grade of $MgO$ , light (technical).		
Molecular Weight:	40.32	
Crystalline Form:	cubic	1
The spec. grade is a fluffy white amorphous powder.		
Color:	colorless	1
Density, g./ml.:	(solid) 3.58	1
Coefficient of Thermal Expansion, linear, 20-500°C:	$12.4 \times 10^{-6}$	
	20-1000°C: $13.7 \times 10^{-6}$	27
	25°C: $14.45 \times 10^{-6}$	97V1
Thermodynamic Data for finely divided $MgO$ :		9
See also Tables a and b		
Heat of Formation, Kcal./mole at 298°K:	-142.95	
See Table a		
Free Energy of Formation, Kcal./mole at 298°K:	-135.31	
Entropy, cal./deg./mole at 298°K:	6.66	
Heat Capacity cal./deg./mole at 298°K:	9.03	
See Table b		

## a. HEAT AND FREE ENERGY OF FORMATION OF $MgO$ (periclase) 2, 8

T, °K	$\Delta H$ (ca. /mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . . .	-143,800 ( + 90)	136,080 ( + 150)
400 . . . . .	-143,810	134,530
500 . . . . .	-143,810	130,860
600 . . . . .	-143,810	128,270
700 . . . . .	-143,800	125,680
800 . . . . .	-143,790	123,680
900 . . . . .	-143,770	120,430
923 . . . . .	-143,766	-119,890
923 . . . . .	-145,920	-115,890
1000 . . . . .	-145,890	-117,730
1100 . . . . .	-145,840	-114,910
1200 . . . . .	-145,750	-112,100
1300 . . . . .	-145,660	-109,300
1393 . . . . .	-145,560	-106,690
1393 . . . . .	-177,060	-106,690
1400 . . . . .	-177,030	-106,350
1500 . . . . .	-176,760	-101,300
1600 . . . . .	-176,380	-96,280
1700 . . . . .	-176,060	-91,300
1800 . . . . .	-175,740	-86,330
1900 . . . . .	-175,420	-81,370
2000 . . . . .	-175,100	-76,400

Magnesium Oxide, MgO (page 2)

Phase Changes of Metal

M.P., 923°K;  $\Delta H = 2160$  cal./g.-atom

B.P., 1393°K;  $\Delta H = 31,500$  cal./g.-atom

Free Energy Equations:

Reaction	Range of Validity, °K	
1) $\text{Mg (c)} + \frac{1}{2} \text{O}_2 = \text{MgO (periclase)}$	298.16-923	
$\Delta F_T^\circ = -144,090 - 1.06T \log T - .13 (10^{-3}T^2) + .25 (10^5T^{-1}) + 29.16T$		
2) $\text{Mg (l)} + \frac{1}{2} \text{O}_2 = \text{MgO (periclase)}$	923-1393	
$\Delta F_T^\circ = -145,810 + 1.84T \log T - .62 (10^{-3}T^2) + .64 (10^5T^{-1}) + 23.07T$		
3) $\text{Mg (g)} + \frac{1}{2} \text{O}_2 = \text{MgO (periclase)}$	1393-2000	
$\Delta F_T^\circ = -180,700 - 3.75T \log T - .62 (10^{-3}T^2) + .64 (10^5T^{-1}) + 65.69T$		
Entropy, cal./deg./mole at 258°K:	6.4	1, 9
See Table b		
Melting Point:	3173°K (2900°C)	9
Heat of Fusion, Kcal./mole:	18.5	9
Boiling Point:	3350 $\pm$ 300°K (3077°C)	8
Heat of Vaporization:	---	
Transition Point:	---	
Heat of Sublimation, Kcal./mole at 298°K:	> 149.4	64

b. HEAT CONTENT AND ENTROPY OF MgO (c)  
(Base, crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	965	2.78	1300 . . . . .	11,310	15.98
500 . . . . .	1975	5.03	1400 . . . . .	12,570	16.92
600 . . . . .	3020	6.94	1500 . . . . .	13,830	17.79
700 . . . . .	4100	8.60	1600 . . . . .	15,090	18.60
800 . . . . .	5225	10.10	1700 . . . . .	16,350	19.36
900 . . . . .	6390	11.47	1800 . . . . .	17,610	20.08
1000 . . . . .	7580	12.73	1900 . . . . .	18,870	20.76
1100 . . . . .	8800	13.89	2000 . . . . .	20,130	21.41
1200 . . . . .	10,050	14.98	2100 . . . . .	21,390	22.02

MgO (c):

Enthalpy:  $H_T - H_{298.15} = 10.18T + 0.87 \times 10^{-3}T^2 + 1.48 \times 10^5T^{-1} - 3690$   
(0.8 percent; 298-2100°K)

Heat Capacity:  $C_p = 10.18 + 1.74 \times 10^{-3}T + 18 \times 10^5T^{-2}$

Heat Capacity, cal./deg./mole: (solid, c) 8 94

See equation above

9

**Magnesium Oxide, MgO (page 3)**

**Decomposition Temperature:** The temperature required to complete dissociation has been estimated to be above that of the temperature of a Bunsen flame. Partial dissociation is said to take place by evaporating a mixture of MgO and metal.

44V27B

**Decomposition Products:** —

**Vapor Pressure:**  $\log_{10} P_{\text{mm.}} = 2.732 \times 10^4/T + 13.13$ , over the temperature range 1800–2200°K

Addnl. Refs.  
1, 3

**X-Ray Crystallographic Data:**

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Molecules/Unit Cell</i>
cubic	$O_h$	4.212	4

97V1

**Hygroscopicity:** Takes up moisture from the air to form  $\text{Mg}(\text{OH})_2$  and  $\text{CO}_2$  from the air to form  $\text{MgCO}_3$ .

**Caution:** Keep container well closed.

29

See also Addnl. Ref. 2.

**Solubility Data:** In water:

.00062 in cold

1

.0086 at 30°C

29

Solubility in water is increased by  $\text{CO}_2$ .

In acids and ammonium salts:

soluble

In alcohol:

insoluble

**Health Hazard:** Inhalation of freshly sublimed MgO may cause metal fume fever. Large doses taken as an antacid may produce undesirable catharsis.

12

29

M.A.C., mg./m.<sup>3</sup> for an 8-hr. day:

15

14

**Safety Classifications:**

OSM:

not listed

ICC:

not listed

**Fire and Explosion Hazard:** —

**Electrostatic Sensitivity:** —

**Use in Pyrotechnics:** MgO is the product of the burning of Mg.

**Additional References:**

- 1) "Stability of Ceramic Materials," J. Wygant and W. Kingrey, Am. Ceram. Soc. Bull. 31, (7) 251 (1952); cited by Ref. 65
- 2) "The Sorption of Water Vapor on Magnesium Oxide," R. Razouk and R. Sh. Mikhail, J. Phys. Chem. 59, 636 (1955)
- 3) "On the Dissociation Energies of Strontium Oxide and Magnesium Oxygen Molecules," R. Porter et al., J. Chem. Phys. 23, 1347 (1955)

# MANGANESE, Mn

Refs.

Specification No.:	JAN-M-476	
The specification covers three grades which differ in purity and granulation. Grade I is intended for delay powder; grades II and III, for pyrotechnics.		
Molecular Weight:	54.94	
Crystalline Form:	cubic or tetragonal	1
Color:	grey-pink	1
Density, g./ml.:	(solid at R.T.) $\alpha = 7.44$ $\beta = 7.29$ $\gamma = 7.21$	37
Coefficient of Thermal Expansion, linear:		
	Temp. ( $^{\circ}\text{C}$ )	Coeff. (cm./cm./ $^{\circ}\text{C}$ )
$\alpha$ phase	-190 to 0	$15.9 \times 10^{-6}$
	-183 to 0	$17.6 \times 10^{-6}$
	0-20	$22.3 \times 10^{-6}$
	0-100	$22.8 \times 10^{-6}$
	0-300	$25.2 \times 10^{-6}$
$\beta$ phase	-183 to 0	$12.8-20.4 \times 10^{-6}$
	0-20	$18.7-24.9 \times 10^{-6}$
$\gamma$ phase	-70 to 0	$13.6 \times 10^{-6}$
	0-20	$14.8 \times 10^{-6}$
Heat of Formation, Kcal./mole at 298 $^{\circ}\text{K}$ :	(gas) 68.34 (c) $\gamma$ , 0.37	1, 5
Free Energy of Formation, Kcal./mole at 298 $^{\circ}\text{K}$ :	(gas) 58.23 (c) $\gamma$ , 0.37	1, 5
Entropy, cal./deg./mole at 298 $^{\circ}\text{K}$ :	(gas) 41.49 (c) $\alpha$ , 7.59 $\gamma$ , 7.72	1
See Tables a, b, c, d		
Melting Point:	1517 $^{\circ}\text{K}$ (1244 $^{\circ}\text{C}$ )	2, 5
Heat of Fusion, cal./mole:	3500	2, 4, 5
Boiling Point:	2314 $^{\circ}\text{K}$ (2041 $^{\circ}\text{C}$ )	5
Heat of Vaporization, cal./mole at 2314 $^{\circ}\text{K}$ :	52,520	5
Transition Points:	(727 $^{\circ}\text{C}$ ) $\alpha \xrightarrow{1000^{\circ}\text{K}} \beta$ (1101 $^{\circ}\text{C}$ ) $\beta \xrightarrow{1374^{\circ}\text{K}} \gamma$ (1137 $^{\circ}\text{C}$ ) $\gamma \xrightarrow{1410^{\circ}\text{K}} \delta$	2, 4, 5
Heat of Transition, cal./mole:	535      545      430 $\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \delta$	2, 4, 5
Heat of Sublimation, cal./mole at 298 $^{\circ}\text{K}$ :	66,730	5
Heat Content or Enthalpy, cal./mole at 298 $^{\circ}\text{K}$ :	See Tables a, b, c, d	
Heat Capacity, cal./mole at 298 $^{\circ}\text{K}$ :	See Tables a, b, c, d	



a. HEAT CONTENT AND ENTROPY OF Mn (c, l)  
(Base,  $\alpha$ -crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	690	1.99	1410 ( $\gamma$ ) . . .	10,330	13.21
500 . . . . .	1385	3.54	1410 ( $\delta$ ) . . .	10,760	13.51
600 . . . . .	2120	4.88	1500 . . . . .	11,780	14.21
700 . . . . .	2895	6.07	1517 ( $\delta$ ) . . .	11,970	14.34
800 . . . . .	3715	7.16	1517 (l) . . .	15,470	16.65
900 . . . . .	4570	8.17	1600 . . . . .	16,380	17.23
1000 ( $\alpha$ ) . . .	5450	9.10	1700 . . . . .	17,480	17.90
1000 ( $\beta$ ) . . .	5985	9.63	1800 . . . . .	18,580	18.53
1100 . . . . .	6820	10.50	1900 . . . . .	19,680	19.12
1200 . . . . .	7795	11.28	2000 . . . . .	20,780	19.69
1300 . . . . .	8715	12.02	2100 . . . . .	21,880	20.22
1374 ( $\beta$ ) . . .	9395	12.53	2200 . . . . .	22,980	20.74
1374 ( $\gamma$ ) . . .	9940	12.93	2300 . . . . .	24,080	21.22
1400 . . . . .	10,220	13.13			

Mn ( $\alpha$ ):

Enthalpy:  $H_T - H_{298.15} = 5.70T + 1.69 \times 10^{-5}T^2 + 0.37 \times 10^{-5}T^{-1} - 1974$   
(0.7 percent; 298–1000°K)

Heat Capacity:  $C_p = 5.70 + 3.38 \times 10^{-5}T - 0.37 \times 10^{-5}T^{-2}$

Mn ( $\beta$ ):

Enthalpy:  $H_T - H_{298.15} = 8.33T + 0.33 \times 10^{-5}T^2 - 2675$  (0.1 percent; 1000–1374°K)

Heat Capacity:  $C_p = 8.33 + 0.66 \times 10^{-5}T$

Mn ( $\gamma$ ):

Enthalpy:  $H_T - H_{298.15} = 10.70T - 4760$  (0.1 percent; 1374–1410°K)

Heat Capacity:  $C_p = 10.70$

Mn ( $\delta$ ):

Enthalpy:  $H_T - H_{298.15} = 11.30T - 5170$  (0.1 percent; 1410–1517°K)

Heat Capacity:  $C_p = 11.30$

## Mn (l):

Enthalpy:  $H_T - H_{298.15} = 11.00T - 1220$  (0.1 percent; 1517–2300°K)

Heat Capacity:  $C_p = 11.00$

Manganese, Mn (page 3)

b. HEAT CONTENT AND ENTROPY OF Mn ( $\gamma$ )  
(Base,  $\gamma$ -crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	705	2.03	1000 . . . . .	5750	9.57
500 . . . . .	1445	3.68	1100 . . . . .	6720	10.50
600 . . . . .	2230	5.11	1200 . . . . .	7730	11.38
700 . . . . .	3050	6.38	1300 . . . . .	8780	12.22
800 . . . . .	3915	7.53	1374 . . . . .	9570	12.81
900 . . . . .	4815	8.59			

Mn ( $\gamma$ ) :

Enthalpy:  $H_T - H_{298.15} = 6.03T + 1.78 \times 10^{-3}T^2 + 0.44 \times 10^{-5}T^3 - 2104$   
(0.1 percent; 298-1374°K)

Heat Capacity:  $C_p = 6.03 + 3.56 \times 10^{-3}T - 0.44 \times 10^{-5}T^2$

c. HEAT CONTENT AND ENTROPY OF Mn (g)  
(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	505	1.46	1900 . . . . .	7960	9.20
500 . . . . .	1005	2.57	2000 . . . . .	8460	9.46
600 . . . . .	1500	3.48	2200 . . . . .	9455	9.93
700 . . . . .	1995	4.24	2400 . . . . .	10,455	10.37
800 . . . . .	2495	4.90	2600 . . . . .	11,465	10.77
900 . . . . .	2990	5.49	2800 . . . . .	12,485	11.15
1000 . . . . .	3490	6.01	3000 . . . . .	13,525	11.51
1100 . . . . .	3985	6.49	3500 . . . . .	16,255	12.35
1200 . . . . .	4480	6.92	4000 . . . . .	19,290	13.16
1300 . . . . .	4980	7.32	4500 . . . . .	22,775	13.98
1400 . . . . .	5475	7.68	5000 . . . . .	26,840	14.84
1500 . . . . .	5970	8.03	6000 . . . . .	36,925	16.67
1600 . . . . .	6470	8.35	7000 . . . . .	49,415	18.59
1700 . . . . .	6965	8.93	8000 . . . . .	63,560	20.48
1800 . . . . .	7465				

Mn (g) :

Enthalpy:  $H_T - H_{298.15} = 4.97T - 1482$  (0.2 percent; 298-3000°K)

Heat Capacity:  $C_p = 4.97$

Manganese, Mn (page 4)

d. HEAT CAPACITY OF Mn:

Solid I, 298-1000°K; Solid II, 1000-1374°K:

Liquid, 1517-2314°K; Gas (monatomic) 2314-3000°K

T, °K	C <sub>p</sub> (cal./deg./mole)	T, °K	C <sub>p</sub> (cal./deg./mole)
298	6.29	1400	10.70
400	6.75	1500	11.30
600	7.54	1600 to	11.00
		2300	
800	8.21	2400	5.02
900	8.60	2600	5.07
1000 to	9.30	2800	5.14
1300		3000	5.25

Decomposition Temperature and Products:

For DTA and TGA see Ref. 33

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp.°C	1292	1505	1666	1792	2029	2151	1260

$$\log P \text{ (atm.)} = 14,848T - 3.028 \log T + 16,489T \text{ (T = abs. temp.)}$$

2.4 mm. at M.P.

X-Ray Crystallographic Data:

System	Space Group	a	c	Atoms/ Unit Cell
cubic (α)	T <sub>d</sub> <sup>2</sup>	8.894		58
cubic (β)	O <sub>h</sub> <sup>2</sup> or O <sub>h</sub> <sup>3</sup>	6.300		20
tetragonal (γ)	D <sub>4h</sub> <sup>17</sup>	3.774	3.526	4
cubic (δ)		3.081 at 1140°C	3.088 at M.P.	

Hygroscopicity (% Gain in weight after 720 hrs. of exposure at 70°F of spec. grade powdered Mn):

R.H., %	50	76	90
Gain, %	0.02	0.34	3.91

Solubility Data: Decomposes water slowly in the cold, rapidly on heating.

Soluble in dilute acids with evolution of hydrogen.

Health Hazard: Inhalation of heavy concentrations of manganese dusts or fumes may produce chronic manganese poisoning. Mn may affect the nervous system and cause paralysis. Mn poisoning is detectable in the blood.

M.A.C., mg./m.<sup>3</sup>:

6

Safety Classifications:

OSM: Class 2, when not packed or stored in the original shipping container or equivalent (dust).

ICC:

not specifically mentioned

**Manganese, Mn (page 5)**

Fire and Explosion Hazard: Powdered manganese metal exposed to air is dangerous fire hazard and when ignited burns with intense heat. Prevent water from contacting the material. Store and process only in build adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction of powdered metal and moisture. In the presence of oxidizing agents powdered Mn is a dangerous fire and explosion hazard. Manganese powder is moderately explosive.	11, 49
Caution: to fight fire, use a special mixture of dry chemical or powdered talc. Use nonsparking tools for repair and maintenance of buildings or equipment where manganese has been stored.	51, 75
Electrostatic Sensitivity: Minimum energy required for ignition of powder by electric sparks (millijoules): $\gamma + 0.77\%$ $\delta + 0.90\%$	26
Minimum explosive concentration of powdered Mn: 125 mg./l.	26
Volume change accompanying phase transformations: $\beta \rightarrow \gamma + 0.77\%$ $\gamma \rightarrow \delta + 0.90\%$	37
Manganese is superficially oxidized on exposure to the air. The $\gamma$ phase (electrolytic Mn) is not attacked by water at ordinary temperatures. It is slightly attacked by steam.	29
Use in Pyrotechnics: as a fuel	

**MANGANESE DIOXIDE,  $\text{MnO}_2$**   
**(Manganese Black, Pyrolusite, Black Oxide of Manganese,**  
**Manganese Peroxide, Manganese Rinoxide, Manganese Superoxide,**  
**Battery Manganese)**

*Refs.*

1, 11, 29

Percent Oxygen:	36.82	
Specification No.:	MIL-M-3281	
Molecular Weight:	86.93	
Crystalline Form:	rhombic or powder	1
Color:	black or brownish-black	1
Density, g./ml.:	(solid) 5.026	
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	-124.5	1, 9
See Table a		
Free Energy of Formation, Kcal./mole at 298°K:	-111.4	1, 9
See Table a		

**a. HEAT AND FREE ENERGY OF FORMATION  $\text{MnO}_2$  (c)**

2

T, °K	$\Delta H$ (cal./mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . .	-124,450 ( $\pm 200$ )	-111,350 ( $\pm 250$ )
400 . . . . .	-124,400	-106,900
500 . . . . .	-124,250	-102,500
600 . . . . .	-124,100	-98,200
700 . . . . .	-123,900	-93,900
800 . . . . .	-123,750	-89,600
900 . . . . .	-123,650	-85,350
1000 . . . . .	-123,500	-81,100

**Free Energy Equation:**

<i>Reaction</i>	<i>Range of Validity, °K</i>
$\text{Mn (s)} + \text{O}_2 \text{ (g)} = \text{MnO}_2 \text{ (c)}$	298.16-1000
$\Delta F_f^\circ = -126,400 - 8.61T \log T + .97 (10^{-6}T^2) + 1.555 (10^6T^{-1}) + 70.14T$	

Entropy, cal./deg./mole at 298°K: 12.7 1, 9

See Table b

Melting Point: 6, 8  
loses oxygen at 1120°K (847°C)  
loses oxygen at 535°C 1

Heat of Fusion: —

Boiling Point: —

Transition Point: —

Heat of Sublimation: —

Manganese Dioxide, MnO<sub>2</sub> (page 2)

b. HEAT CONTENT AND ENTROPY OF MnO<sub>2</sub> (c)  
(Base, crystals at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	1445	4.16	700 . . . . .	6415	13.36
500 . . . . .	3020	7.67	800 . . . . .	8185	15.73
600 . . . . .	4685	10.70			

MnO<sub>2</sub> (c) :

Enthalpy:  $H_T - H_{298.15} = 16.60T + 1.22 \times 10^{-3}T^2 + 3.88 \times 10^5T^{-1} - 6359$   
(0.1 percent; 298-800°K)

Heat Capacity:  $C_p = 16.60 + 2.44 \times 10^{-3}T - 3.88 \times 10^5T^{-2}$

Heat Capacity, cal./deg./mole: (solid) 12.91

9

Decomposition Temperature, °K: 1120

8

For DTA see Ref. 33

Decomposition Products: Loses O when heated; the temperature of decomposition varying with the method of preparation from 530°C down to even 200°C. The resulting products being successively Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, and MnO. The reactions are reversible.

50V8

Dissociation Pressure:  $2 \text{ MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 (\text{s}) + \frac{1}{2} \text{ O}_2 (\text{g})$

42V7

Press. atm.	0.030	0.164	0.263	0.209	1.36	1.000
T, °K	655.1	721.1	751.1	803.1	809.1	1213.1

see also 91

X-Ray Crystallographic Data:

1

System	Space Group	a	c	Molecules/Unit Cell
tetragonal	D <sub>4h</sub> <sup>14</sup>	4.44	2.89	2

Hygroscopicity:

Solubility Data: In water, HNO<sub>3</sub>, cold H<sub>2</sub>SO<sub>4</sub>, acetone:

insoluble  
soluble

1

In HCl with evolution of Cl:

Health Hazard: Continued or prolonged inhalation or exposure to heavy concentrations of MnO<sub>2</sub> dusts or fumes may cause chronic manganese poisoning. The chief site of damage is the central nervous system. Although toxic when freshly formed, the dry crystals or powder are normally considered an eye irritant and toxic only in large quantities. In solution, manganese dioxide forms a strong base that may burn the skin, and is very irritating to the eyes.

12, 50V5

M.A.C., mg./m.<sup>3</sup>:

6

14

Safety Classifications:

OSM: Class 1. Class 2 when not packed or stored in original shipping containers or equivalent.

ICC:

oxidizing material

Coast Guard:

hazardous material

**Manganese Dioxide, MnO<sub>2</sub> (page 3)**

**Fire and Explosion Hazard:** A strong oxidizer and a fire hazard in the finely divided state. Should not be heated or rubbed with organic matter or other oxidizable substances such as sulfur, sulphides, phosphides or hypophosphites. 29

**Precautions When Handling Manganese Dioxide:**

Work carefully when handling bulk manganese dioxide to avoid excessive "dusting." Keep work areas clean, and wash hands frequently. Store away from readily oxidizable materials such as powdered metals, oils, acids, or organic solvents.

A solution of one part vinegar to four parts water by volume is an effective neutralizer, and may be safely used in the eyes or on any part of the skin. Take a victim to a physician immediately for examination and further treatment.

**Electrostatic Sensitivity:**

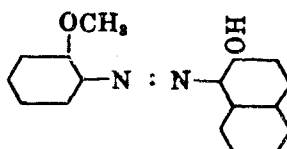
Use in Pyrotechnics:

as an oxidizer

17

**1-(2-METHOXYPHENYLAZO)-2-NAPHTHOL**  
 (2-anisole-azo-betanaphthol, Sudan Red G, Brilliant Fat Scarlet R,  
 C.I. 12150, C.I. Solvent Red 1, C.I. Food Red 16)

Formula:  $C_{17}H_{14}N_2O_2$



Specification No.:	MIL-D-3179	
The spec. covers two grades differing in purity (grade I, 90% ; grade II, 80%) and granulation.		
Molecular Weight:	278.32	
Crystalline Form:	needles	
Color:	shiny reddish-yellow	88V16
Density, g./ml.:		
Apparent Density (spec. grade I)	min. 0.30, max. 0.70	
Coefficient of Thermal Expansion:	—	
Heat of Formation:	—	
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	451°K (178°C)	88V16
Spec. grade II, min.	448°K (175°C)	
Heat of Fusion:	—	
Boiling Point:	—	
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy	—	
Heat Capacity:	—	
Decomposition Temperature:	—	
Decomposition Products:	—	
Vapor Pressure:	—	
X-Ray Crystallographic Data:	—	
Hygroscopicity:	—	
Solubility Data:		48, 88V16
In water, alkalis:	insoluble	
In benzene and cold alcohol:	difficult	
In alcohol:	red solution on boiling	
In $CHCl_3$ and benzene:	fairly soluble	
In conc. $H_2SO_4$ :	soluble with violet-red color	

Refs.

48A



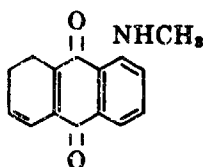
**1-(2-Methoxyphenylazo)-2-Naphthol (page 2)**

Health Hazard:	toxicity unknown	92
Spec. requires each container be conspicuously labeled, "Caution—Avoid Skin Contact. Use Adequate Ventilation."		
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard:	_____	
Electrostatic Sensitivity:	_____	
Use in Pyrotechnics:	to color smoke mixtures red	

# 1-METHYLAMINOANTHRAQUINONE

(1-N-methylaminoanthraquinone, Celliton Pink R, Duranol Red GN, C.I. 60505, C.I. Disperse Red 9)

Formula:  $C_{15}H_{11}NO_2$



Refs.

84, 48A

Specification No.:	MIL-D-3824	
Spec. covers two grades differing in granulation.		
Molecular Weight:	237.11	
Crystalline Form:	needles	88V14
Color:	yellow-red	84
Density, g./ml.:		
Apparent Density:	(Spec) $0.35 \pm .15$	
Coefficient of Thermal Expansion:	—	
Heat of Formation:	—	
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	443°K (170°C)	84
Spec. grade II, min.:	442°K (169°C)	
Heat of Fusion:	—	
Boiling Point:	—	
Heat of Vaporization, Kcal./mole at 25°C and 1 atm.:	$28.4 \pm 0.7$	Addnl. Ref. 3
Entropy of Vaporization, vapor at 1 atm., cal./mole/°C:	$52.87 \pm 0.30$	Addnl. Ref. 1
Heat of Sublimation: Kcal./mole:	30.85	Addnl. Ref. 1
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature:		
For TGA see Ref. 80		
Decomposition Products:	—	
Vapor Pressure: $\log_{10} P$ (cm Hg) = $\frac{a}{T} + b$		Addnl. Ref. 1
$a = -6740$ ; $b = 13.435 \pm 0.036$ ; $T = \text{abs. temp.}$		
Energy of Activation for Volatilization (97% purity), Kcal./mole at 297-376°C:	19.5	80
X-Ray Crystallographic Data:	—	
Hygroscopicity:	—	

5) J. Soc. Dyers Colourists 70, 68-77 (1954)

# MOLYBDENUM, Mo

Refs.

Molecular Weight: 95.95  
 Crystalline Form: cubic  
 Color: silvery-white metal,  
 grey-black powder  
 Density: (solid) 10.22  
 10.24  
 9.01

1A

1A

94

66A

31A

Coefficient of Thermal Expansion, linear:

Temp, °C	Coeff. $\times 10^6$
20-149	5.43
20-482	5.19
20-649	5.36
20-982	5.80
20-1316	6.28
20-1593	6.65
	4.9

94

50V9

$$L = L_0 [1 + (5.01t + 0.00138t^2) \times 10^{-6}]$$

at 20°C:  $4 \times 10^{-6}$

31A

See also Refs. 49A (curve of temp. vs. coeff.), 66A, and Addnl. Refs.

Heat of Formation, Kcal./mole at 298°K: (g) -155.5

9, Addnl.

Ref. 1

Free Energy of Formation, Kcal./mole at 298°K: (g) -144.2

9, 31A

Entropy, cal./deg./mole at 298°K: (g) 43.462  
 (c) 6.83

9

5, 9, 94, 97

## a. HEAT CONTENT AND ENTROPY OF Mo (c, l)

(Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	595	1.71	1900	11,200	12.27
500	1205	3.06	2000	12,040	12.70
600	1825	4.20	2100	12,900	13.12
700	2460	5.17	2200	13,770	13.53
800	3100	6.02	2300	14,670	13.92
900	3750	6.79	2400	15,580	14.31
1000	4410	7.49	2500	16,510	14.69
1100	5090	8.13	2600	17,460	15.06
1200	5790	8.74	2700	18,420	15.42
1300	6510	9.31	2800	19,400	15.70
1400	7250	9.85	2890 (c)	20,290	16.09
1500	8000	10.38	2890 (l)	26,940	18.39
1600	8780	10.88	2900	27,040	18.43
1700	9570	11.36	3000	28,040	18.77
1800	10,380	11.82			

Mo (c) :

$$H_T - H_{298.15} = 5.18T + 0.83 \times 10^{-5}T^2 - 618 \quad (0.5 \text{ percent; } 298-2890^\circ\text{K})$$

$$C_p = 5.18 + 1.68 \times 10^{-5}T$$

Molybdenum, Mo (page 2)

Mo (l) :

$$H_T - H_{298.15} = 10.00T - 1960 \text{ (0.1 percent; 2890-3000°K)}$$

b. HEAT CONTENT AND ENTROPY OF Mo(g)  
(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	505	1.46	1500 . . . . .	5975	8.03
500 . . . . .	1005	2.57	1600 . . . . .	6470	8.35
600 . . . . .	1500	3.48	1700 . . . . .	6975	8.66
700 . . . . .	1995	4.24	1800 . . . . .	7475	8.94
800 . . . . .	2495	4.91	1900 . . . . .	7980	9.22
900 . . . . .	2990	5.49	2000 . . . . .	8490	9.48
1000 . . . . .	3485	6.01	2200 . . . . .	9530	9.97
1100 . . . . .	3985	6.49	2400 . . . . .	10,600	10.44
1200 . . . . .	4480	6.92	2600 . . . . .	11,710	10.88
1300 . . . . .	4980	7.32	2800 . . . . .	12,880	11.31
1400 . . . . .	5475	7.69	3000 . . . . .	14,115	11.74

Mo (g) :

$$H_T - H_{298.15} = 4.97T - 1482 \text{ (0.1 percent; 298-1800°K)}$$

$$H_T - H_{298.15} = 3.56T + 0.40 \times 10^{-5}T^2 - 230 \text{ (0.2 percent; 1800-3000°K)}$$

$$C_p = 3.56 + 0.80 \times 10^{-5}T$$

$$H_T - H_{298.15} = 5.48T + 0.65 \times 10^{-5}T^2 - 1692 \text{ (± 1 percent; 298-1800°K)}$$

$$C_p = 5.48 + 1.30 \times 10^{-5}T$$

Melting Point, °C: 2620 ± 10

Heat of Fusion, cal./mole at 2890°K: 6.6 ± 0.7

Boiling Point, °C: 4800  
4825

Considerably higher values are also given.

See Vapor Pressure

Heat of Vaporization, Kcal./mole: 128.42 31A  
117.4 94  
121.0 ± 9.0 97

Transition Point, °K: 2883 1A

Heat of Transition, Kcal./mole: 5.8 1A

Heat of Sublimation, Kcal./mole at 298° K: 157.5 5

Heat Content or Enthalpy, cal./mole at 298°K: (solid) 1092 5

See Tables a and b

Heat Capacity, cal./deg./mole: (solid) 5.61 (liquid) 10.00 31A  
6.29  
(gas) 4.968 at 25° 5, 31A

See Tables a and b

**Molybdenum, Mo (page 3)**

Decomposition Temperature: oxidized to MoO<sub>3</sub> at red heat 29

Decomposition Products: —

Vapor Pressure:

Press. atm.	$3.9 \times 10^{-10}$	$1.7 \times 10^{-5}$	$8.6 \times 10^{-4}$	$1.8 \times 10^{-1}$	1.0	94
Temp. °C	1727	2610	3227	4727	5560	

$\log P_{\text{mm.}} = -31,060T^{-1} - 0.2 \log T 9.41$  (bet. 298°K and M.P.) 97  
1 mm. at 3102°C 12

See also Refs. 64V1 and 66A

X-Ray Crystallographic Data:

System	Space Group	a	Molecules/Unit Cell	Addnl. Ref. 1
cubic	O <sub>h</sub>	3.1403 at 20° 3.1468 at 25°	2	49A

Hygroscopicity: —

Solubility Data: Not attacked by water, dilute acids, or concd. HCl. Practically insol. in alkali hydroxides or fused alkalies. Sol. in hot concd. HNO<sub>3</sub>, hot concd. H<sub>2</sub>SO<sub>4</sub>, in fused KClO<sub>3</sub> or KNO<sub>3</sub>. 29, 1A

Ref. 94 gives some corrosion data in several acids.

Health Hazard: probably slight 12  
M.A.C., mg./m.<sup>3</sup>: 15 12

Safety Classifications:

OSM: not listed

ICC: not listed

Fire and Explosion Hazard: moderate 12, 96

Dust may react explosively with air. Sub-200 mesh dust has little or no explosive hazard. In fighting fire use powdered graphite, dolomite, sodium chloride, etc., not water.

Heat of Combustion, cal./g.: 1810 49A

Electrostatic Sensitivity: —

Use in Pyrotechnics: as a fuel

Additional References:

- 1) "Molybdenum," L. Northcott, Academic Press, Inc., New York (1956)
- 2) Ref. 49A
- 3) Ref. 64V1

**MOLYBDENUM TRIOXIDE, MoO<sub>3</sub>**  
(Molybdic Anhydride, Molybdite)

Percent Oxygen:	33.34	
Specification No.:	not listed	
Molecular Weight:	143.95	
Crystalline Form:	rhombic	1A
Color:	white to yellowish or colorless	1A
Density, g./ml.:	(solid) 4.50 at 19.5°C 4.692 at 21°C	1A 29
Coefficient of Thermal Expansion, cubic:	21-78°C $7 \times 10^{-6}$ 78-195°C $5 \times 10^{-6}$ 195-273°C $3 \times 10^{-6}$	44S53
Heat of Formation, Kcal./mole at 298°K:	(c) -180.33 -178.2 ± 1.5	1A, 9 97
Free Energy of Formation, Kcal./mole at 298°K:	(c) -161.95	1A, 9

**a. HEAT AND FREE ENERGY OF FORMATION OF MoO<sub>3</sub> (c, l)**

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16 . . . .	-180,300 (± 1500)	-162,000 (± 1600)
400 . . . . .	-180,100	-155,700
500 . . . . .	-179,700	-149,600
600 . . . . .	-179,200	-143,700
700 . . . . .	-178,700	-137,800
800 . . . . .	-178,200	-132,000
900 . . . . .	-177,600	-126,200
1000 . . . . .	-177,000	-120,600
1068 . . . . .	-176,600	-116,700
1068 . . . . .	-164,600	-116,700
1100 . . . . .	-164,200	-115,200
1200 . . . . .	-163,000	-110,800
1300 . . . . .	-161,800	-106,500
1400 . . . . .	-160,600	-102,300
1500 . . . . .	-159,500	-98,200

**Free Energy Equations:**

Reaction	Range of Validity, °K	
1) Mo (c) + 3/2 O <sub>2</sub> (g) = MoO <sub>3</sub> (c)	298.16-1068	2
Δ F° = -182,650 - 8.86T log T - 1.55 × 10 <sup>-8</sup> T <sup>2</sup> + 1.54 × 10 <sup>5</sup> T <sup>-1</sup> + 90.07T		
2) Mo (c) + 3/2 O <sub>2</sub> (g) = MoO <sub>3</sub> (l)	1068-1500	1A, 9
Δ F° = -179,770 - 36.34T log T + 1.40 × 10 <sup>-8</sup> T <sup>2</sup> - 0.30 × 10 <sup>5</sup> T <sup>-1</sup> + 167.61T		
Entropy, cal./deg./mole at 298°K:	18.68	

**Molybdenum Trioxide, MoO<sub>3</sub> (page 2)**

**b. HEAT CONTENT AND ENTROPY OF MoO<sub>3</sub> (c, l)**

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	1935	5.56	1068 (c) . . .	17,670	28.26
500 . . . . .	4035	10.24	1068 (l) . . .	30,170	39.96
600 . . . . .	6260	14.30	1100 . . . . .	31,200	40.92
700 . . . . .	8570	17.86	1200 . . . . .	34,400	43.70
800 . . . . .	10,940	21.02	1300 . . . . .	37,600	46.26
900 . . . . .	13,390	23.91	1400 . . . . .	40,800	48.63
1000 . . . . .	15,920	26.57	1500 . . . . .	44,000	50.84

**MoO<sub>3</sub> (c) :**

$$H_T - H_{298.15} = 20.73T + 2.59 \times 10^{-5}T^2 + 4.18 \times 10^5T^{-1} - 7813 \text{ (0.1 percent; 298-1068°K)}$$

$$C_p = 20.73 + 5.18 \times 10^{-5}T - 4.18 \times 10^5T^{-2}$$

**MoO<sub>3</sub> (l) :**

$$H_T - H_{298.15} = 32.00T - 4000 \text{ (0.1 percent; 1068-1500°K)}$$

**Melting Point, °C:**

795

1A, 24A

797

Addnl. Ref. 2

Melts to a dark yellow liquid, which solidifies to a yellowish-white crystalline mass.

**Heat of Fusion, Kcal./mole:**

11.91

2

12.54

6

**Boiling Point, °K:**

1530 ± 50

6, 8

The following values are also given :

1100°C

24A

1428°K

41

**Heat of Vaporization, Kcal./mole:**

33

9, 41

**Temperature of Sublimation, °K:**

(gas) 973

52

volatile above 500°C

94

sublimes about 700°C

**Heat of Sublimation, Kcal./mole at 691°C:**

65

9, 41

68.1

Addnl. Ref. 3

**Heat Content or Enthalpy:**

See Table b

**Heat Capacity, cal./deg./mole:**

(liquid) 32.0

2

See Table b

**Decomposition Temperature:**

—

For DTA see Ref. 33

**Decomposition Products:**

—



**Molybdenum Trioxide, MoO<sub>3</sub> (page 3)**

**Vapor Pressure:**

Press. mm.	.009	0.05	0.30	1.75	10.1	23.4	105.1	288.3	476.2	760	44S53
Temp. °C	610	650	700	750	800	850	950	1050	1100	1155	

$$298^{\circ}\text{K to M.P.: } \log p_{\text{mm.}} = -15,230 - 4.02 \log T + 27.16$$

$$\text{M.P. to B.P.: } \log p_{\text{mm.}} = 12,480T^{-1} - 4.02 \log T + 24.60$$

24A

24A

**X-Ray Crystallographic Data:**

System	Space Group	a	Molecules/Unit Cell	
cubic	V <sub>h</sub> <sup>18</sup>	3.14103 at 25°	4	18, 44S53

**Hygroscopicity:**

—

**Solubility Data:**

In water, g./100 ml. at 18°C:

0.1066

1A

at 70°C:

2.055

In acids, NH<sub>4</sub>OH, alkalies, sulfur:

soluble

In acids after strong ignition:

very slightly soluble

29

**Health Hazard:**

probably slight

12

L.D., g./kg.:

400

29

**Safety Classifications:**

OSM:

not listed

ICC:

not listed

**Fire and Explosion Hazard:**

—

**Electrostatic Sensitivity:**

—

Use in Pyrotechnics: Product of the burning of Mo and some of its compounds.

**Additional References:**

- 1 Ref. 7
- 2) C.A. 53, 20992 (1959)
- 3) C.A. 48, 13396 (1954)

# NICKEL, Ni

Refs.

Specification No.: JAN-N-412A

The standard A.S.T.M. grades of virgin nickel are:

Electrolytic	99.5% Ni
X shot	98.9% Ni
A shot	97.75% Ni
Ingot	98.5% Ni

16

Molecular Weight:	58.71	
Crystalline Form:	cubic	1
Color:	silvery metal	1
Density, g./ml.:	(solid) 8.90	1
Coefficient of Thermal Expansion, 16-250°C:	$13.97 \times 10^{-6}$	1

Temperature °C

Coeff.

-19 to + 16

$10.12 \times 10^{-6}$

40

$12.79 \times 10^{-6}$

375-1000

$13.46 \times 10^{-6}$

25-100

$12.9 \times 10^{-6}$

Heat of Formation, Kcal./mole at 298°K: (gas) -101.260 5

Free Energy of Formation, Kcal./mole at 298°K: (gas) -90.413

Entropy, cal./deg./mole at 298°K: (gas) 43.52 5  
(solid) 7.14 5

See Tables a and b

Melting Point: 1728°K (1455°C) 1

Heat of Fusion, cal./mole: 4210 4, 5

Boiling Point: 3110°K (2837°C) 5

Heat of Vaporization, cal./mole: 88,870 5

Transition Point:  $\alpha$  to  $\beta$  at 633°K (360°C) 4

Heat of Transition, cal./mole:  $\alpha$  to  $\beta$ , 0 4

Heat of Sublimation, cal./mole at 298°K: 101,260 5

Heat Content or Enthalpy, cal./mole: (solid) 1144 5  
(gas) 1631

See Tables a and b

## a. HEAT CONTENT AND ENTROPY OF Ni (c, l) (Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	665	1.91	900	4445	8.03
500	1380	3.51	1000	5210	8.84
600	2180	4.96	1100	5985	9.58
633 ( $\alpha$ )	2460	5.42	1200	6780	10.27
633 ( $\beta$ )	2460	5.42	1300	7600	10.93
700	2940	6.14	1400	8450	11.56
800	3690	7.14	1500	9320	12.16

Nickel, Ni (page 2)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
1600 . . . . .	10,210	12.73	2200 . . . . .	19,910	18.08
1700 . . . . .	11,110	13.28	2400 . . . . .	21,750	18.88
1725 ( $\beta$ ) . . .	11,330	13.40	2600 . . . . .	23,590	19.62
1725 (l) . . .	15,540	15.84	2800 . . . . .	25,430	20.30
1800 . . . . .	16,230	16.24	3000 . . . . .	27,270	20.93
2000 . . . . .	18,070	17.21	3200 . . . . .	29,110	21.52

Ni ( $\alpha$ ):

Enthalpy:  $H_T - H_{298.15} = 4.06T + 3.52 \times 10^{-5}T^2 - 1523$  (0.3 percent; 298–633°K)

Heat Capacity:  $C_p = 4.06 + 7.04 \times 10^{-5}T$

Ni ( $\beta$ ):

Enthalpy:  $H_T - H_{298.15} = 6.00T + 0.90 \times 10^{-5}T^2 - 1701$  (0.2 percent; 633–1725°K)

Heat Capacity:  $C_p = 6.00 + 1.80 \times 10^{-5}T$

Ni (l):

Enthalpy:  $H_T - H_{298.15} = 9.20T - 330$  (0.1 percent; 1725–3200°K)

b. HEAT CONTENT AND ENTROPY OF Ni (g)

(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	575	1.66	1900 . . . . .	9310	10.77
500 . . . . .	1150	2.94	2000 . . . . .	9865	11.05
600 . . . . .	1740	4.01	2200 . . . . .	10,970	11.58
700 . . . . .	2335	4.93	2400 . . . . .	12,065	12.06
800 . . . . .	2930	5.73	2600 . . . . .	13,155	12.49
900 . . . . .	3525	6.43	2800 . . . . .	14,235	12.89
1000 . . . . .	4120	7.06	3000 . . . . .	15,310	13.26
1100 . . . . .	4715	7.62	3500 . . . . .	17,985	14.09
1200 . . . . .	5300	8.13	4000 . . . . .	20,665	14.80
1300 . . . . .	5885	8.60	4500 . . . . .	23,370	15.44
1400 . . . . .	6465	9.03	5000 . . . . .	26,135	16.02
1500 . . . . .	7040	9.43	6000 . . . . .	31,940	17.08
1600 . . . . .	7615	9.80	7000 . . . . .	38,305	18.06
1700 . . . . .	8185	10.14	8000 . . . . .	45,415	19.01
1800 . . . . .	8750	10.46			

Ni (g):

Enthalpy:  $H_T - H_{298.15} = 5.99T + 0.36 \times 10^{-5}T^2 - 1907$  (0.3 percent; 298–1000°K)

Heat Capacity:  $C_p = 5.99 + 0.36 \times 10^{-5}T$

Enthalpy:  $H_T - H_{298.15} = 6.07T - 0.11 \times 10^{-5}T^2 - 4120$  (0.4 percent; 1000–4500°K)

Heat Capacity:  $C_p = 6.07 - 0.22 \times 10^{-5}T$

**Nickel, Ni (page 3)**

Heat Capacity, cal./deg./mole at 298°K: (solid) 6.23  
(liquid) 9.20  
(gas) 5.58

4, 5

**c. HEAT CAPACITY OF Ni**  
(Solid, 298–1728°K; liquid, 1728–3000°K)

5

T, °K	C <sub>p</sub> (cal./deg./mole)
298	6.23
500	7.47
800	7.44
1200	8.16
1600	8.88
1700	9.06
1800–3000	9.20

See equations above

Decomposition Temperature: —

Decomposition Products: —

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	1810	2057	2234	2364	2603	2732	1452

1

**X-Ray Crystallographic Data:**

System	Space Group	a	c	Atoms/ Unit Cell
(α) hexagonal	D <sub>6h</sub>	2.65	4.32	2
(β) cubic	O <sub>h</sub>	3.517		4

1

Hygroscopicity: Nonhygroscopic. Not affected by water.

29

**Solubility Data:**

1, 29

In water, fused alkalis or NH<sub>3</sub>: insoluble  
In dilute HNO<sub>3</sub>: soluble  
In HCl or H<sub>2</sub>SO<sub>4</sub>: slightly soluble

**Health Hazard:** Exposure to nickel may cause dermatitis (Nickel itch) in sensitive individuals. Ingestion of large amounts (even 1-3 mg./kg. of body weight) causes nausea, vomiting, diarrhea, depression of the central nervous system, and myocardial damage. Its health hazard is, however, considered slight.

12, 25, 29

M.A.C., mg./m.<sup>3</sup>: 0.5

25

**Safety Classifications:**

OSM: class 2

ICC: Listed under "Explosives and Other Dangerous Materials." Classed as a flammable solid; red label.

**Nickel, Ni (page 4)**

**Fire and Explosion Hazard:** Ni dust is explosive and a dangerous fire hazard. It has an ignition temperature above 700°C, and burns with intense heat. When compounded with oxidizing agents the powdered metal is a dangerous fire and explosion hazard. It decomposes steam at red heat. The amount of powdered metal which may become involved in a fire should be strictly limited. Fires must not be fought with ordinary streams of water because of the danger of liberating large quantities of hydrogen gas. Fires involving small amounts of powdered Ni may be fought with fog nozzles or special extinguishing powders.

12, 14, 49

In the repair or maintenance of buildings or equipment, powder or dust should be reduced and nonsparking tools used. Store and process only in rooms or buildings adequately ventilated at the highest point.

**Electrostatic Sensitivity:**

not ignited by electric sparks

49

**Use in Pyrotechnics:**

as a fuel

## NITROCELLULOSE (12.6% N)

(Cellulose Nitrate, Pyrocellulose, Pyro, Nitro Cellulose, Nitrocotton)

Formula:  $[C_6H_{10-x}O_5-x(ONO_2)_x]_n$

Where  $x$  = no. of  $ONO_2$  groups and  $n$  = degree of polymerization. For 12.6% N,  $x = 2.45$ .

Specification No.:

JAN-N-244

The spec. lists four grades of which Grade A, with  $12.60 \pm 0.10\%$  N, is used for pyrotechnics.

Molecular Weight: Variable, approx.  $0.42$  to  $0.78 \times 10^6$  or  $272.3 n$  (calculated from formula)

Form: Cotton-like fibrous solid or amorphous powder (when cut up or beaten).

Color:

white

Density, g./ml.:

(solid) about 1.66

Coefficient of Thermal Expansion, linear:

$9-16 \times 10^{-5}$

Heat of Formation, cal./g.

-617

Free Energy of Formation:

—

Entropy:

—

Melting Point: Decomposes. In a vacuum melts at approx.  $473^\circ K$  ( $200^\circ C$ ) before exploding.

Heat of Fusion:

—

Boiling Point:

decomposes

Transition Point:

—

Heat of Sublimation:

—

Heat Content or Enthalpy:

—

Heat Capacity:

—

Decomposition Temperature: See Addnl. Refs. 1, 2, 3, 4

For DTA see Ref. 33

Decomposition Products: Depend on conditions of decomposition.

Vapor Pressure:

Press. mm.	0.0	0.0
Temp. $^\circ C$	25	60

X-Ray Crystallographic Data:

for cellulose trinitrate  
( $x = 3$ )

System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell
monoclinic		13.9	25.6	9.6	$\beta = 90^\circ$	

Hygroscopicity, g.  $H_2O$ /100 g. N.C.:

$\frac{334.3 - 23.65 N}{31.11 - N}$  (approx.)

or more roughly 14.6 - N % nitrogen  
at 30° and 90% R.H., %:

3

Refs.

Addnl. Ref. 1

1

Addnl. Ref. 1

31

13

Addnl. Ref. 2

13

Addnl. Ref. 1

Addnl. Ref. 1

13

**Nitrocellulose (12.6% N) (page 2)**

**Solubility Data:** Numerous substances dissolve or more accurately disperse pyrocellulose. Among these are acetone, ether-alcohol (2:1), fatty acid esters, nitro compounds, and organic nitrates.  
in water, ether, and benzene: insoluble

Addnl. Ref. 1

**Safety Classifications:**

OSM: Class 12 when wet with 8-30% water.

ICC: Listed under "Explosives and Other Dangerous Materials," as a high explosive when dry and as a flammable liquid when dispersed in a solvent; red label.

**Fire and Explosion Hazard:** Dry nitrocellulose is extremely sensitive to shock and friction, and very dangerous when ignited, even in the open, or when heated with oxidizing agents. Dry nitrocellulose burns in an instantaneous flash. Wet nitrocellulose is less hazardous. Nitrocellulose when impure is subject to spontaneous ignition. Storage of dry nitrocellulose is not permitted as it has all the hazards of a sensitive and easily ignited high explosive. It is stored wet (25-30% water) in zinc-lined boxes or metal drums. Must contain not less than 20% moisture by weight when shipped. Caution: keep away from heat and open flame.

12, 14

Flash Point, closed cup, °F: 40

12

Impact Sensitivity, 2 kg. wt.:

13

Bur. of Mines Apparatus, cm.:

8 (10% point)

Sample weight, mg.:

3 (10% point)

P.A. Apparatus, in.:

5

**Explosion Temperature Test:**

5 second point 170°C with decomposition

13

**Electrostatic Sensitivity:** Readily accumulates static charges when dry.

14

**Volatility at 60°C, micrograms/cm.<sup>2</sup>/hr.:**

0

13

**Oxygen Balance to CO<sub>2</sub>, %:**

-35

to CO, %:

0.6

**Vacuum Stability Test, 5 g. sample**

Temp. °C	90	100	120
cc. 40 hrs.	0.17	1.0	
cc. 16 hrs.			11.+

**200 Gram Bomb Sand Test, 0.4 g. sample**

Grams sand crushed to pass a 30-mesh sieve: 45.0

**Sensitivity (initiator required for complete detonation)**

Lead azide:

0.10 g.

**Heat of Combustion, cal./g.:**

2409

**Heat of Explosion, cal./g.:**

855

**Gas Volume on Explosion, cc./g.:**

919

**Second Order Transition Temperature, °C:**

(approx.) 66

59

(nitrogen content not mentioned):

**Use in Pyrotechnics:** For coating compositions to reduce the penetration of moisture, and as a bonding agent.

20

**Nitrocellulose (12.6% N) (page 3)**

**Additional References:**

- 1) "Cellulose Nitrate," F. D. Miles, Oliver and Boyd, London and Edinburgh. Interscience Publishers, Inc., New York (1955)
- 2) "The Spontaneous Ignition of Nitrocellulose," E. K. Rideal and A. J. B. Robertson, Third Symposium on Combustion and Flame and Explosion Phenomena, The Williams & Wilkins Company, Baltimore (1949)
- 3) "Cellulose and Cellulose Derivatives," E. Ott et al., Eds., Interscience Publishers, Inc., New York (1954-55)
- 4) "The Kinetics of Thermal Decomposition of Nitrocellulose," R. W. Phillips et al., J. Phy. Chem. 59, 1034 (1955)



## PARLON

(Chlorinated Rubber, Tornesit, Alloprene. Parlon is trademarked  
by Hercules Powder Co.)



**Formula:** Rubber chlorinated polyisoprene  $[-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2]_x$  chlorinated approximately 67% Cl by weight.

Chlorination of rubber results in a complete reaction. There is not only addition and substitution of chlorine but also cyclization along the polymer chains. The theoretical chlorine content for the completely chlorinated isoprene unit,  $\text{C}_5\text{H}_4\text{Cl}_4$ , is 68.5%. Parlon is marked in five viscosity types. Stabilized Parlon usually contains 1% of an epoxy compound as a stabilizer to improve resistance to heat, ultraviolet light and moisture. Sunlight causes discoloration and embrittlement in unpigmented, unstabilized films. Parlon is resistant to dampness, soaps, molds, and mildew.

**Molecular Weight:** Variable (high) depending on viscosity.

**Crystalline Form:** Coarse amorphous inelastic powder; poorly crystallized, granular powder.

**Color:**

white (color of film,  
water-white)

**Density, g./ml.:**

(solid) 1.56 (also given as  
1.64 and up)

**Coefficient of Thermal Expansion:**

$12-13 \times 10^{-5}$

**Heat of Formation:**

—

**Free Energy of Formation:**

—

**Entropy:**

—

**Melting Point, softening point of film:**

413°K (140°C)

**Heat of Fusion:**

—

**Boiling Point:**

—

**Transition Point:**

—

**Heat of Sublimation:**

—

**Heat Content or Enthalpy:**

—

**Heat Capacity:**

—

**Decomposition Temperature:**

Effect of dry heat on film (continuous exposure) stable up to 125°C. Appreciable decomposition at 135°C.

**Decomposition Products:**

—

**Vapor Pressure:**

—

**X-Ray Crystallographic Data:**

—

**Hygroscopicity:** Moisture content as shipped is less than 0.5%.

Absorbs little moisture on storage.

Moisture absorption at 80% R.H. in 24 hr., %: 0.14

Water vapor transfer of free film, g./100 sq. in./mil. in 24 hr. at 95°F and 100% R.H.: 1.0

**Refs.**

59

**Addnl. Ref. 1**

59, 60, Addnl.  
Refs. 1, 2

59, Addnl.  
Ref. 1

**Addnl. Ref. 1**  
60

**Addnl. Ref. 1**

**Addnl. Ref. 1**

**Addnl. Ref. 1**

**Parlon (page 2)**

**Solubility Data:** Soluble in  $\text{CCl}_4$ , esters, aromatic hydrocarbons, and ketones. Unaffected by strong or weak acids or alkalies, salt spray, aliphatic alcohols, and aliphatic hydrocarbons. Insoluble in acetone alone.

59, 60, Addnl.  
Ref. 1

**Health Hazard:** nontoxic

**Safety Classifications:**

OSM: not listed

ICC: not listed

**Fire and Explosion Hazard:** Nonflammable. Will ignite in the flame of a bunsen burner, but the flame is selfextinguishing. On burning, it melts, gives off bubbles of gas and chars.

59, 60

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:** As a color intensifier and binder. Used in rapid drying paints.

59, 60, Addnl.  
Ref. 1

**Additional References:**

- 1) "Parlon, Properties and Uses," Hercules Powder Co., Inc., Wilmington, Del. (1957)
- 2) "Rubber, Polyisoprenes, and Allied Compounds. Part IV. The Relative Tendencies towards Substitutive and Additive Reaction during Chlorination," G. F. Bloomfield, J. Chem. Soc. 1943, 289

### Refs.

**JAN-P-670**

**Molecular Weight:**

(red, P) 30.974

## 4.5

## 1.5

**1, 5, 16, 29,**

**Addnl. Ref. 1**

**Density, g./ml.:**

(solid) yellow. 1.82

red. 2.20

**black, 2.70**

**Coefficient of Thermal Expansion, linear, 0–44°C:**

 $124 \times 10^{-8}$ 

Heat of Formation, Kcal./mole at 298°K:

(gas) 75.18

**Free Energy of Formation, Kcal./mole at 298°K:**

(gas) 66.71

white (c) 0.000

red (c)-4.4

**black (c) -10.3**

**Entropy, cal./deg./mole at 298°K:**

**white (c) 10.6**

red (c) 5.46

**See Tables a to e**

**Melting Point:**

white ( $\alpha$ ) 317.4°K

(44.3°C)

red, 870°K (597°C)

**Heat of Fusion, cal./mole:**

**white, 150**

### Boiling Point:

**white, 554°K (218°C)**

red, 280°K (7°C)

(ignites in air)

**Phosphorus, P<sub>4</sub> (yellow), P (red) (page 2)**

**Transition Points and Heats of Transition:**

Form		Temp. of Transition	Heat of Transition
Initial	Final	°K	Kcal./mole
c, IV	c, III	30.31	0.0197
c, III	c, II	49.44	0.186
c, II	c, I	88.12	0.116

I = black, II = red, III and IV = white

(β-white transforms to α-white at -76.9°C)

Heat of Sublimation, cal./mole at 298°K:

(white to P<sub>4</sub> gas) 14,100  
(red to P<sub>4</sub> gas) 30,820  
(P<sub>2</sub> gas) 42,725  
(P gas) 79,800

Addnl. Ref. 2

5

**a. HEAT CONTENT AND ENTROPY OF P (red)**

(Base, crystals at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	620	1.79	700 . . . . .	2690	5.62
500 . . . . .	1270	3.24	800 . . . . .	3440	6.62
600 . . . . .	1970	4.51			

**P (red) :**

Enthalpy:  $H_T - H_{298.15} = 4.74T + 1.95 \times 10^{-5}T^2 - 1587$  (0.3 percent; 298-800°K)

Heat Capacity:  $C_p = 4.74 + 3.90 \times 10^{-5}T$

**b. HEAT CONTENT AND ENTROPY OF P<sub>4</sub> (white, I)**

(Base, crystals at 298.15°K)

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
317.4 (c) . .	434	1.41	370 . . . . .	2270	6.90
317.4 (I) . .	1034	3.30	400 . . . . .	2975	8.74
350 . . . . .	1800	5.60			

**P<sub>4</sub> (white) :**

Enthalpy:  $H_T - H_{298.15} = 22.50T - 6708$  (0.1 percent; 298-317.4°K)

Heat Capacity:  $C_p = 22.50$ ;  $\Delta H_{317.4}$  (fusion) = 600

**P<sub>4</sub> (I) :**

Enthalpy:  $H_T - H_{298.15} = 23.50T - 6425$  (0.1 percent; 314.7-400°K)

Heat Capacity:  $C_p = 23.50$

Phosphorus, P<sub>4</sub> (yellow), P (red) (page 3)

c. HEAT CONTENT AND ENTROPY OF P (g)  
(Base, ideal gas at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400	505	1.46	1900	7975	9.21
500	1005	2.57	2000	8480	9.47
600	1500	3.48	2200	9500	9.96
700	1995	4.24	2400	10,535	10.41
800	2495	4.90	2600	11,590	10.83
900	2990	5.49	2800	12,670	11.23
1000	3490	6.01	3000	13,780	11.61
1100	3985	6.49	3500	16,685	12.51
1200	4480	6.92	4000	19,790	13.34
1300	4980	7.32	4500	23,070	14.11
1400	5475	7.69	5000	26,495	14.83
1500	5975	8.03	6000	33,605	16.13
1600	6470	8.35	7000	40,825	17.24
1700	6970	8.65	8000	47,980	18.20
1800	7475	8.94			

P (g):

Enthalpy:  $H_T - H_{298.15} = 4.97T - 1.482$  (0.1 percent; 298-2000°K)

d. HEAT CONTENT AND ENTROPY OF P<sub>2</sub> (g)  
(Base, ideal gas at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400	800	2.31	1000	5910	10.06
500	1620	4.14	1200	7660	11.65
600	2450	5.65	1400	9430	13.02
700	3300	6.96	1600	11,200	14.20
800	4160	8.11	1800	12,970	15.24
900	5030	9.13	2000	14,750	16.18

P<sub>2</sub> (g):

Enthalpy:  $H_T - H_{298.15} = 8.31T + 0.23 \times 10^{-5}T^2 + 0.72 \times 10^{-8}T^3 - 2740$   
(0.4 percent; 298-2000°K)

Heat Capacity:  $C_p = 8.31 + 0.46 \times 10^{-5}T - 0.72 \times 10^{-8}T^2$

Phosphorus, P<sub>4</sub> (yellow), P (red) (page 4)e. HEAT CONTENT AND ENTROPY OF P<sub>4</sub> (g)  
(Base, ideal gas at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400	1710	4.93	1300	18,900	27.21
500	3500	8.92	1400	20,860	28.67
600	5360	12.31	1500	22,830	30.03
700	7240	15.21	1600	24,800	31.30
800	9150	17.76	1700	26,770	32.50
900	11,080	20.03	1800	28,740	33.62
1000	13,020	22.07	1900	30,720	34.69
1100	14,980	23.94	2000	32,690	35.70
1200	16,940	25.65			

P<sub>4</sub> (g):Enthalpy:  $H_T - H_{298.15} = 18.93T + 0.43 \times 10^{-5}T^2 + 2.81 \times 10^{-8}T^{-1} - 6625$   
(0.2 percent; 298-1500°K)Heat Capacity:  $C_p = 18.93 + 0.86 \times 10^{-5}T - 2.81 \times 10^{-8}T^{-2}$ 

Heat Capacity, cal./deg./mole at 298°K: (gas) 4.96

See tables above

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp °C (yellow)	76.6	128.0	166.7	197.3	251.0	280.1	44.1
(black)	290	338	371	393	432	453	
(violet)	237	287	323	349	391	417	590

X-Ray Crystallographic Data:

System	Space Group	a	b	c	Unit Cell Molecules/
red, black (rhombic)	V <sub>16</sub>	3.31	4.38	10.50	8
(yellow) (cubic) (at 35°C)		7.17			16 (4P <sub>4</sub> )

(Crystalline and amorphous black and red P give similar X-ray patterns)

Hygroscopicity, Red P at 70°F and 216 hr. exposure:

R.H.	50	76	90
Gain in wt., %	2.04	5.0	11.06

Solubility Data:

Yellow or White

H<sub>2</sub>O: 0.0003 g./ml. at 15°C  
slight in hot

Alcohol: 0.3 g./100 ml.

CS<sub>2</sub>: 880 g./100 ml. at 10°C

Red

very slight  
insol. in hot water  
slight in abs. alc.  
insol. in CS<sub>2</sub>, ether, NH<sub>3</sub>

**Phosphorus, P<sub>4</sub> (yellow), P (red) (page 5)**

Benzene: 1 g. in 35 ml.  
CHCl<sub>3</sub>: 1 g./40 ml.  
Olive oil: 1 g./80 ml.  
Oil of Turpentine: 1 g./60 ml.  
Sl. sol. in NH<sub>3</sub>, alkalies, ether

**Health Hazard:** Yellow phosphorus is poisonous even when ingested in small amounts. An approximate fatal dose is 50 mg. Phosphorus fumes are also very poisonous. External contact may cause severe burns. Long continued absorption can cause necrosis of the jaw bone and chronic poisoning. Phosphorus is especially dangerous to the eyes. 12, 29

M.A.C. (yellow phosphorus), mg./m.<sup>3</sup>: 0.1 14

Red phosphorus is poisonous on inhalation or ingestion but slower acting than yellow phosphorus. It should never be allowed to come in contact with the eyes. 12, 93

Phosphorus poisoning is detectable in the urine. 12

**Safety Classifications:**

OSM: Class not specified. As a fire hazard it should be listed in class 1.

ICC: Flammable solid; yellow label.

U.N. Phosphorus, white or yellow, dry, or under water, or in solution is classified as an inflammable solid, liable to spontaneous combustion.

**Fire and Explosion Hazard:** On exposure to air white phosphorus (WP) bursts into flame and is thus a serious fire hazard. Containers or ammunition containing WP should be kept below its M.P. or 44.1°C, as pressure may rupture the container. Phosphorus is preferably stored under water in sealed metal vessels enclosed in wooden boxes or metal drums. WP is dangerous when heated with oxidizing agents, as it emits highly toxic fumes of oxides of phosphorus. Use water to fight fire. Red phosphorus, while less reactive than yellow phosphorus, is a dangerous fire hazard. It is easily ignited by spark or friction and is dangerous when in contact with organic materials or oxidizers. It can ignite spontaneously in air. It emits highly toxic fumes when heated. 12, 14

**Autoignition Temperature, in air, °F:** (yellow) 86 75, 29  
(red, amor.) 500 67, 71

**Use in Pyrotechnics:** As a fuel, in incendiary and smoke compositions.

**Additional References:**

- 1) "Two New Modifications of Phosphorus," P. W. Bridgman, J. Am. Chem. Soc. 36, 1344 (1914)
- 2) "Phosphorus and Its Compounds," Vol. I, J. R. Van Wazer, Interscience Publishers, Inc., New York (1958)

## PLURONIC F 68

Following information comes from the Wyandotte Chemicals Corporation, Wyandotte, Michigan, manufacturers of Pluronic F 68.

Pluronic F 68 is a block-polymer prepared by adding propylene oxide to the two hydroxyl groups of a propylene glycol nucleus. The resulting hydrophobic base can be made to any desired length, varying from 800 to many thousands in molecular weight. By adding ethylene oxide to this hydrophobic base, it is possible to put polyoxyethylene hydrophilic groups on the end of the molecule. These hydrophilic groups can be controlled in length to constitute anywhere from 10 to 90% of the final molecule. The simplified structure can be represented as  $\text{HO}(\text{CH}_2\text{-CH}_2\text{-O})_n(\text{CH}_2\text{-CH}_2\text{O})_m(\text{CH}_2\text{-CH}_2\text{O})_p\text{.H}$ .



Pluronic F 68 is a flake with a hydrophobic base molecular weight of approximately 1750; 80% of the molecule, by weight, consists of hydrophilic polyoxyethylene groups and the remaining 20%, hydrophobic polyoxypropylene groups. The total molecular weight of F 68 =  $\frac{1750}{.20} = 8750$ .

pH of 2.5% aqueous solution:

7

Cloud Point:

of aqueous solutions in concentrations up to 60.0%:

at 70% concentration:

> 100°C  
semi-solid

of 10% aqueous solutions at pH 2 and 10

in 4% NaOH:

> 100°C

40 % concentration:

semi-solid

20% concentration:

26.5°C

100% concentration:

38.5°C

1% concentration:

47°C

Solubility in Organic Solvents at 25°C in g./100 ml. solvent:

Samples of 0.1, 1.0, 5.0, and 10.0 g. were dissolved in 100 ml. of solvent and observed after 30 min. for any phase separations, turbidity, etc.

Ethyl alcohol (95%):

> 10.0

Toluene:

5.0

Perchloroethylene:

insol.

Kerosene:

insol.

Ethylene glycol:

insol.

Vegetable oil:

insol.

Mineral oil:

insol.

Surface Tension at 25°C, dynes/cm.:

1.0% solution

41.9

0.1% solution

45.6

0.01% solution

49.9

0.001% solution

54.3

Using a DuNuoy Tensiometer, samples are in aqueous solutions at the specified concentrations.

Concentration Required for a 25 sec. Draves Sink Time:

At both 25° and 50°C, the maximum concentration evaluated was 5 g./l. At this concentration the sink time was 300 seconds.

Use in Pyrotechnics: A surface acting agent used as a detergent, emulsifier, and wetting agent.



## POLYCHLOROTRIFLUOROETHYLENE (Kel-F Brand Oils and Waxes)

Refs.

KEL-F oils and waxes are low molecular weight polymers of chlorotrifluoroethylene ( $\text{CF}_2 = \text{CFCl}$ ) which constitute a homologous series of compounds composed of chlorotrifluoroethylene repeating units and terminal chlorine atoms. This series is referred to as "whole telomer." KEL-F oils and waxes are made by Minnesota Mining and Manufacturing Co.

All data from  
Addnl.  
Ref. 1

Formula:  $\text{Cl}-(\text{CF}_2-\text{CFCl})_x\text{Cl}$

Specification No.: MIL-M-55028A

Molecular Weight: From 303 for the lowest boiling (dimeric) component of #1 oil to 5-10,000 for the highest melting ingredients of #200 wax.

Color: All KEL-F oils and waxes are colorless and odorless. In the liquid state all products are clear and free from sediment. At room temperature the oils are transparent, and the waxes take on a translucent or opaque white appearance.

Specific Gravity: KEL-F oils are comparatively dense, with values approaching twice the density of water. The waxes are generally greater than twice the density of water at temperatures less than  $25^\circ\text{C}$ . Specific gravity depends less markedly on temperature than does viscosity.

Vapor Pressure: Because of their low heats of vaporization and weak intermolecular forces, the oils and waxes are characterized by relatively high vapor pressures. Values can be calculated by means of the vapor pressure constants and equation in the table of typical properties. (See below).

Solubility: The oils and waxes are soluble in aromatic, aliphatic, and chlorinated hydrocarbons, alcohols, ketones, esters and fluorocarbons; and insoluble in water and mineral acids. The degree of solubility varies widely with molecular weight; the waxes are less soluble than the oils.

Viscosity: KEL-F oils are available in three viscosity grades (1, 3, 10 centistokes at  $210^\circ\text{F}$ ). #40 wax, by virtue of its low melting point, can also be considered as an extra-heavy oil (viscosity = 40 cs. at  $210^\circ\text{F}$ ). Viscosities of halofluorocarbon liquids depend markedly on temperature.

### TYPICAL PROPERTIES OF STANDARD KEL-F OILS AND WAXES

	Grade Designation					
	1	3	10	40	10-200	200
Molecular Weight	500	630	780	940	—	—
Clarity (R.T.)	clear	clear	clear	opaque	opaque	opaque
Refractive Index, $n_D$						
77°F	1.400	1.405	1.410	—	—	—
160°F	—	—	—	1.398	1.401	—
Viscosity, centipoises						
100°F	2	25	220	—	—	—
210°F	0.8	3	10	40	55	—
266°F	—	—	—	—	—	145
Viscosity, centipoises						
100°F	3.6	47	425	—	—	—
210°F	—	5	13	75	105	—

**Polychlorotrifluoroethylene (page 2)**

	Grade Designation					
	1	3	10	40	10-200	200
Viscosity, Temp. Coeff. <sup>1</sup>	0.67	0.88	0.96	—	—	—
Pour Point, °F	<-70	-45	+30	+90	—	—
Melting Point, ASTM, D-127°F	—	—	—	100	150	200
Specific Gravity						
68°F/39°F	1.84	1.93	1.96	—	2.02	2.11
100°F/39°F	1.81	1.90	1.93	—	1.99	—
160°F/39°F	—	1.85	1.88	1.92	1.94	—
Vapor Pressure Constants <sup>2</sup>						
A	7.4991	8.4976	9.0503	10.2123	9.6116	—
B	2351	3161	3743	4863	4313	—
Heat of Vaporization						
cal./g.	21	23	22	23	—	—
Kcal./mole	10.7	14.5	17.1	22	—	—
Surface Tension, dynes/cm.	23	28	30	—	—	—
Specific Heat, cal./g.	—	—	0.22	—	—	—
Thermal Conductivity						
BTU/hr./ft. <sup>2</sup> /°F/ft.	—	—	0.080	0.110	—	—
Heat of Formation, cal./g. <sup>3</sup>	-1200	-1200	-1200	-1200	-1200	-1200

<sup>1</sup> V.T. Coeff. = 1-Vis at 210°F/Vis at 100°F

<sup>2</sup> log P (mm. Hg) = A-B/T°K

<sup>3</sup> calculated

**Dielectric Properties:** The oils and waxes have very good electrical properties. The dielectric strength of KEL-F oil (0.100 in. gap) is 500 volts/mil. The volume resistivity is in excess of 10<sup>14</sup> ohm-cm.

**Corrosivity:** The oils and waxes are noncorrosive, in themselves, towards metals. Storage in nickel, monel, mild steel, stainless steel, and even aluminum offers no problems under ambient conditions. However, the oils are not rust-inhibiting, and therefore moisture should be excluded from containers.

**Chemical Stability:** KEL-F oils and waxes are extremely stable against the attack of strong acids, alkalies, and oxidants. No reaction has been observed with permanganate, chromic acid, fuming nitric acid, or hydrogen peroxide. The oils are not attacked by ClF<sub>3</sub> at 300°F, concentrated H<sub>2</sub>SO<sub>4</sub> at 400°F, or concentrated aqueous alkali at the boiling point. Oxygen and ozone do not react appreciably with KEL-F oils; indeed there is evidence that the oils are even more chemically stable in the presence of oxygen. Under stringent oxidizing conditions (2000 psig. O<sub>2</sub> at 300°F for 8 hr.) tests have shown no change in KEL-F oil alone or in contact with a variety of metals. Nor is there any effect on the metals themselves, including copper. *Caution: Softer metals such as aluminum and magnesium may react vigorously with KEL-F oils under conditions of high shear, where fine particles of fresh metal are exposed.*

**Health Hazard:** The oils and waxes are substantially nontoxic and physiologically inert. However, thermal decomposition products at extremely elevated temperatures (600°F) are toxic and adequate ventilation under these conditions is strongly recommended.

**Polychlorotrifluoroethylene (page 3)**

**Fire and Explosion Hazard:** Because of their high fluorine and chlorine content, the KEL-F oils and waxes do not support combustion—that is, they are self-extinguishing once the igniting source is removed.

**Infrared Transmission:** As halofluorocarbons are substantially free of hydrogen, the KEL-F oils and waxes are transparent in the 2-4 micron infrared region, where most organic liquids are strongly absorbing.

**Use in Pyrotechnics:** Oxidizing agent in pyrotechnic compositions.

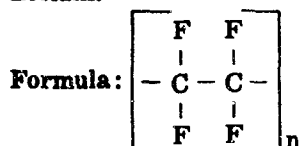
**Additional References:**

- 1) "KEL-F Brand Halofluorocarbon Oils, Waxes, Greases and Alkanes," Minnesota Mining and Manufacturing Company (1958)

## POLYTETRAFLUOROETHYLENE

(Teflon, Fluon, Fluoroflex, Polytetrafluoroethylene Resin)

Teflon is a thermoplastic, homopolymer composed of long chains of  $-\text{CF}_2-$  units. Its useful temperature range is  $-75^\circ$  to  $+250^\circ\text{C}$ . It cannot be molded, but at  $205^\circ\text{C}$  it can be extruded. It is not wetted or affected by water, neither does it stick to anything. Teflon is the term used in the U.S. and Fluon in Great Britain.



Where n is unknown (see Molecular Weight).

Specification No.:

PA-PD-614

Covers one type of general purpose molding or extruding material and the quality of the final molded or extruded parts. The applicable A.S.T.M. Specifications and Test Methods are D1457, D257, D150, D638, D785, D256, D792, D648, D696, D543, D542.

Molecular Weight: Unknown; estimated at 500,000 or more and possibly many millions.

Form and Color: Colorless to grey powder, flakes, or grains. Transparent in thin sheet. Teflon is highly crystalline with no appreciable cross linking. A degree of crystallinity of 93-97% has been calculated for the polymer with a density of 2.296. Teflon is available as film, laminations, powder (pellets or granules), rods or tubes (extruded), or sheets. It is fabricated by extrusion, hot forming or drawing, compression molding, and injection molding.

Density, g./ml.:

(solid) 2.1-2.3

Coefficient of Thermal Expansion, linear:

$5.5 \times 10^{-5}$

Below  $15^\circ$  and above  $25^\circ\text{C}$  the cubical coefficients of expansion are roughly of the same order,  $3 \times 10^{-4}$  cc./cc./ $^\circ\text{C}$ , but at about  $20^\circ\text{C}$  there is a 1% increase in volume, presumably due to a change in crystal structure.

Heat of Formation, Kcal./monomole at  $298^\circ\text{K}$ :

(estimated for particular sample used)

-193.5

-199

Free Energy of Formation:

Entropy, Enthalpy, and Heat Capacity:

Form	Temp. $^\circ\text{C}$	Entropy abs.j. $^\circ\text{K}^{-1}\text{g}^{-1}$	Enthalpy abs.j. $\text{g}^{-1}$	Heat Capacity* abs.j. $^\circ\text{K}^{-1}\text{g}^{-1}$
powder	280	1.005	140.5	1.036
	310	1.134	178.6	0.9959
molded	280	1.019	144.6	1.012
	310	1.137	179.3	1.021
annealed	280	1.011	142.9	0.9761
	310	1.135	179.4	1.023

\*Experimental data show that the heat capacity of a Teflon sample varies with its mechanical and thermal history.

Refs.

29, 60

29

1

40, 68

68, 1

1

1, 10,

Addnl.

Ref. 12

Addnl.

Ref. 10

Addnl.

Ref. 7

Addnl. Refs.

14, 15

Addnl. Ref.

11

**Polytetrafluoroethylene (page 2)**

Melting Point: (softening) 600°K  
(327 ± 5°C)

Heat of Fusion: —

Boiling Point: above 673°K (400°C)

Spec., 68

Teflon begins to evaporate without melting.

Heat of Polymerization, Kcal./mole of monomer: -47

40

**Transition Point and Phase Changes:**

Teflon crystallizes in two forms. A first order phase change occurs at about 292°K (19°C) and melts at 600°K (327°C). A second order transition, involving the crystalline phase, occurs at about 303°K (30°C). This is not related to the glass transition which has not been located in this polymer, but it must be below 173°K (-100°C) as the polymer is still flexible at this temperature.

Addnl. Ref.  
14

68

Addnl. Ref. 3,  
9, 10, 11,  
12, 13

Heat of Sublimation: —

**COMPARISON OF THE ENTHALPY AND ENTROPY CHANGE  
IN THE INTERVAL 280-310°K**

Sample and run	$\Delta H$	$\Delta S$
Teflon powder:	abs.j.g <sup>-1</sup>	abs.j°K <sup>-1</sup> g <sup>-1</sup>
Run 4 .....	38.02	0.1293
Run 6 .....	38.04	0.1294
Molded Teflon:		
Run 3 .....	34.68	0.1177
Run 4 .....	34.75	0.1180
Annealed Teflon:		
Run 2 .....	36.42	0.1236
Run 4 .....	36.53	0.1240
Quenched Teflon:		
Run 2 .....	35.49	0.1205

Addnl.  
Ref. 11

Specific Heat, cal./deg./g.: 0.28

Above 40°C (powdered):  $C_p = 0.2227 + 2.50 \times 10^{-4}t$  (°C)

(drawn)  $C_p = 0.2227 + 2.39 \times 10^{-4}t$  (°C)

Addnl. Ref. 7  
Addnl. Ref. 8

Decomposition Temperature: about 400°C

1

**Decomposition Products:**

Depolymerizes to the monomer. Above 750°F decomposition liberates F. The polymer decomposes at elevated temperatures. In a vacuum, the monomer is the chief product. At low temperatures (250-350°C) degradation seems to start at the chain ends. at higher temperatures random cleavage becomes more important. In air degradation is more complicated, giving off extremely toxic products. Teflon decomposes slowly above 525°F.

68, 70, 60.  
Addnl. Refs.  
2, 4, 5

Vapor Pressure at 25°C, mm.:  $1 \times 10^{-7}$

Addnl. Ref. 6

In the equation  $\log p_{\text{mm.}} = A - B/T$ ,  $A = 4.3$ , and  $B = 3400$  over the range 300-450°K.

**Polytetrafluoroethylene (page 3)**

**X-Ray Crystallographic Data:**

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell</i>
pseudohexagonal		5.54	5.54	16.8	$\gamma = 119.5$	high temp. form 15 low temp. form 13

The chain repeat distance is 2.62A.

**Hygroscopicity:**

nonhygroscopic

**Solubility Data:** There is no known solvent or plasticizer for Teflon. It is unaffected by strong acids, even aqua regia, and by strong alkalies. However, prolonged contact with fluorine, hot plasticizers, and polymeric waxes should be avoided.

**Health Hazard:** Heated to decomposition it gives off toxic fumes of F and F compounds.

**Safety Classifications:**

OSM:

not listed

ICC:

not listed

**Fire and Explosion Hazard:**

nonflammable

**Electrostatic Sensitivity:**

—

**Mechanical Properties:**

Modulus of elasticity,  $10^8$  psi:

33-65

Tensile strength, psi:

1500-3000

Ultimate elongation, %:

120-350

Yield stress, psi:

1600-2000

Yield strain, %:

50-70

Rockwell hardness:

J 75-J 95

Notched Izod impact test:

2.5-4.0

**Refractive Index:**

1.585-1.600

**Use in Pyrotechnics:** To make inert seals or containers for pyrotechnic compositions, and as an oxidizing agent.

**Additional References:**

- 1) Nature 174, 549 (1954)
- 2) D. K. Harris, The Lancet, 1008 (1951)
- 3) C. E. Weir, J. Research NBS 50, 95 (1953)
- 4) S. L. Madorsky et al., ibid. 51, 327 (1953)
- 5) R. E. Florin et al., ibid. 53, 121 (1954)
- 6) "Vapor Pressure of Plastic Materials," N. Jensen, J. Appl. Phys. 27, No. 12 (1956)
- 7) "Combustion Calorimetry of Organic Fluorine Compounds," W. Good et al., J. Phys. Chem. 60, 1080 (1956)

68  
Addnl. Ref. 1  
40

Addnl.  
Ref. 10  
PA-PD-614  
29, 40

12, Addnl.  
Ref. 2

1

1

**Polytetrafluoroethylene (page 4)**

- 8) "Specific Heat of Synthetic High Polymers. V. A Study of the Order-Disorder Transition of Polytetrafluoroethylene," P. Marx and M. Dole, *J. Am. Chem. Soc.* **77**, 4771 (1955)
- 9) *Structural Reports* **12**, 367-68 (1949)
- 10) "A Room Temperature Transition in Polytetrafluoroethylene," H. Rigby and C. W. Bunn, *Nature* **164**, 583 (1949)
- 11) "Calorimetric Properties of Polytetrafluoroethylene (Teflon) from 0° to 365°K," G. Furukawa et al., *J. Research NBS* **49**, 273 (1952)
- 12) *C.A.* **52**, 15118 (1958)
- 13) *C.A.* **52**, 12516 (1958)
- 14) "Thermal Stability of Polytetrafluoroethylene," C. R. Patrick, *Nature* **181**, 698 (1958)
- 15) "Thermochemical Studies of Fluorocarbons," H. C. Duus, *Ind. Eng. Chem.* **1445** (1955)

POLYVINYLCHLORIDE, PVC		Refs.
(Exon, Geon, Koroseal, Marvinol, Pliovic, Tygon, Velon, Vinylite, Vygen, Agilide)		59, 60
Formula: Approximately $(-\text{CH}_2\cdot\text{CHCl}\cdot\text{CHCl})_n$ , where $n = \text{about } 4000$		59
A variable polymer. Specification calls for $56 \pm 1\% \text{ Cl}$		
Specification No.:	MIL-P-20307 (includes Army Spec. No. 50-11-147)	
Molecular Weight:	variable, approximately 250,000	59
Crystalline Form:	(spec. grade) powder	
In PVC, units of the polymer chains are arranged essentially head-to-tail. In addition there may be some branching as a result of chain transfer during polymerization. Solid PVC is only slightly crystalline.		68
Color:	colorless to amber	1
Density, g./ml.:	(solid) unplasticized 1.4	59
Specification, Apparent Density:	$0.5 \pm 0.1 \text{ g./ml.}$	Addnl. Ref. 1
Coefficient of Thermal Expansion, linear:	$5-6 \times 10^{-5}$	Addnl. Refs. 1, 8
Heat of Formation, Kcal./mole at $25^\circ\text{C}$ , per monomer unit:	$22.6 \pm .3$	Addnl. Ref. 7
Free Energy of Formation:	—	
Entropy:	—	
Melting Point: Variable, depending on degree of polymerization. Begins to soften between $343^\circ$ and $353^\circ\text{K}$ ( $70^\circ$ and $80^\circ\text{C}$ ). High molecular weight polymers do not flow well enough for practical molding below $423^\circ\text{K}$ ( $150^\circ\text{C}$ ). Second order transition temperature approx. $348^\circ\text{K}$ ( $75^\circ\text{C}$ ).		59, Addnl. Refs. 8, 6
Heat of Fusion:	—	
Boiling Point:	—	
Transition Point:	see Melting Point	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature: For TGA see Addnl. Ref. 9		
Decomposition Products:	HCl and darkening	
PVC begins to break down even as low as $150^\circ\text{F}$ . It is also unstable to light, darkening as HCl is evolved. Stability to both heat and light can be greatly improved by the addition of stabilizers. As the loss of HCl appears to be autocatalytic, the stabilizers used are usually mild alkalies, alkali or alkali earth oxides and hydroxides, fatty acid salts, or HCl acceptors; e.g., acetylene oxide compounds. Alcoholates, carbonates, amines and many compounds have been found to be effective stabilizers. These can be used alone or in combination to adjust the properties of the plastic in the direction desired, e.g., flexibility, improved flame resistance.		59



**Polyvinylchloride, PVCl (page 2)**

Vapor Pressure: ———

X-Ray Crystallographic Data: Partly crystalline; fiber period  $5.0 \pm .05$  Å or a multiple of 5.0 Å

Hygroscopicity, Specification Grade Material: Gain in mg./g. at R.T. after exposure in static and vacuum desiccators:

Time, days	65% R.H.		75% R.H.		86% R.H.		93% R.H.	
	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.	Stat.	Vac.
1	0.1	0.1	0.3	0.3	0.5	0.1	0.7	0.2
7	0.5	0.3	0.2	0.1	0.3	0.5	0.7	0.2
30			0.1		0.1		0.1	

Solubility Data: Insoluble in acids and alkalis. Soluble in cyclohexanone, methylcyclohexanone, nitrobenzene, dimethylformamide, tetrahydrofuran, isophorone, mesityl oxide. Low molecular weight PVCl is soluble in higher alkylketones, dioxane, methylene chloride.

Health Hazard: ———

Safety Classifications:

OSM:

not listed

ICC:

not listed

Fire and Explosion Hazard: Self extinguishing. Decomposition by heat liberates HCl.

Heat of Combustion, cal./g. ( $H_2O$  liquid) at  $25^\circ$ : 4374.9

Electrostatic Sensitivity: ———

Use in Pyrotechnics: As a retardant, color intensifier, and bonding agent.

**Additional References:**

- 1) "Linear and Stereoregular Addition Polymers," N. Gaylord and H. Mark, Interscience Polymers. Vol. 2 (1959)
- 2) "The Structures and Properties of some Pyrolyzed Polymers," F. H. Winslow et al. (Paper given June 1955.) Paper in the Proceedings of the Second Conference on Carbon held at the University of Buffalo, Buffalo, N.Y. (1956)
- 3) "The Investigation of Synthetic Linear Polymers by X-Rays," C. S. Fuller, Chem. Revs. 26, 143 (1940)
- 4) "Infrared Spectra of Thermally Degraded Poly Vinyl Chloride," R. Stromberg et al., J. Research NBS 60, No. 2, 147 (1958)
- 5) "Characterization of Organic Substances by Differential Thermal Analysis," H. Morita and H. M. Rice, Analytical Chemistry 27, 336 (1955)
- 6) "Specific Heat of Synthetic High Polymers. VI. A Study of the Glass Transition in Polyvinyl Chloride," S. Alford and M. Dole, J. Am. Chem. Soc. 77, 4774 (1955)
- 7) "Heats of Combustion of Some Organic Compounds Containing Chlorine," G. C. Sinke and D. R. Stull, J. Phys. Chem. 62, 397 (1958)
- 8) C.A. 52, 15118 (1958)
- 9) Anal. Chem. 27, 336 (1955)

Addnl. Ref. 3

32

59

59, 60

Addnl. Ref. 7

# **POTASSIUM, K** (Kalium)

*Refs.*

Specification No.:		
Molecular Weight:	39.100	
Crystalline Form:	cubic	1
Color:	silvery metal	1
Density, g./ml.:	(solid) 0.87 <sup>20°</sup>	1
Coefficient of Thermal Expansion, linear at 0-50°C:	$85 \times 10^{-6}$	27
Heat of Formation, Kcal./mole at 298°K:	(monatomic gas) 21,420 (diatomic gas) 30,580	5
Free Energy of Formation, Kcal./mole at 298°K:	(monatomic gas) 14,589 (diatomic gas) 21,965	5
Entropy, cal./deg./mole at 298°K:	(monatomic gas) 38.30 (diatomic gas) 59.67 (c) 15.39	5
See tables below		
Melting Point:	336.4°K (63.3°C)	4, 5
Heat of Fusion, cal./mole:	558	
Boiling Point:	1039°K (766°C)	5
Heat of Vaporization, cal./mole:	18,530	5
Transition Point:	—	
Heat of Sublimation, cal./mole at 298°K:		
to ideal monatomic gas:	21,420	5
to ideal diatomic gas:	30,580	
Heat Content or Enthapy, cal./mole:	(solid) 1695	5
See tables below		
Heat Capacity, cal./deg./mole:	(solid) 7.16 (liquid) 7.80 (gas) 4.97	4, 5

See tables below

## **a. HEAT CONTENT AND ENTROPY OF K (c, l)** (Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
336.4 (c) . . .	286	0.90	700 . . . . .	3515	7.97
336.4 (l) . . .	844	2.56	800 . . . . .	4225	8.92
400 . . . . .	1330	3.89	900 . . . . .	4940	9.76
500 . . . . .	2075	5.55	1000 . . . . .	5665	10.53
600 . . . . .	2805	6.88	1100 . . . . .	6400	11.23

**K (c) :**

Enthalpy:  $H_T - H_{298.15} = 1.34T + 9.70 \times 10^{-5}T^2 - 1262$  (0.1 percent; 298-336.4°K)

Heat Capacity:  $C_p = 1.34 + 19.40 \times 10^{-5}T$

Potassium, K (page 2)

K (l) :

Enthalpy:  $H_T - H_{298.15} = 7.06T - 0.70 \times 10^5 T^{-1} - 1323$  (0.3 percent; 336.4–1100°K)

Heat Capacity:  $C_p = 7.06 + 0.70 \times 10^5 T^{-2}$

4

b. HEAT CONTENT AND ENTROPY OF K (g)  
(Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	505	1.46	1900	7965	9.21
500	1005	2.57	2000	8465	9.46
600	1500	3.48	2200	9475	9.94
700	1995	4.24	2400	10,490	10.39
800	2495	4.90	2600	11,525	10.80
900	2990	5.49	2800	12,580	11.19
1000	3490	6.01	3000	13,660	11.56
1100	3985	6.48	3500	16,540	12.45
1200	4480	6.92	4000	19,810	13.32
1300	4980	7.32	4500	23,750	14.25
1400	5475	7.69	5000	28,720	15.29
1500	5975	8.03	6000	42,950	17.87
1600	6470	8.35	7000	62,210	20.83
1700	6970	8.65	8000	82,400	23.53
1800	7465	8.94			

K (g) :

Enthalpy:  $H_T - H_{298.15} = 4.97T - 1482$  (0.1 percent; 298–2000°K)

c. HEAT CONTENT AND ENTROPY OF K<sub>2</sub>(g)  
(Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	925	2.67	1600	12,240	15.65
500	1840	4.71	1700	13,215	16.24
600	2760	6.29	1800	14,200	16.80
700	3685	7.82	1900	15,180	17.33
800	4615	9.06	2000	16,170	17.84
900	5550	10.16	2100	17,165	18.33
1000	6490	11.15	2200	18,165	18.79
1100	7440	12.05	2300	19,170	19.24
1200	8390	12.88	2400	20,180	19.67
1300	9345	13.65	2500	21,195	20.08
1400	10,305	14.36	2750	23,760	21.06
1500	11,270	15.02	3000	26,350	21.96

Potassium, K (page 3)

$K_2(g)$  :

Enthalpy:  $H_T - H_{298.15} = 8.91T + 0.26 \times 10^{-3}T^2 - 2680$  (0.1 percent; 298-3000°K)

Heat Capacity:  $C_p = 8.91 + 0.52 \times 10^{-3}T$

For tables of thermodynamic values see Ref. 5

Decomposition Temperature: —

Decomposition Products: —

Vapor Pressure:

Press. mm.	1	10	40	100	400	760
Temp. °K	341	443	524	586	708	774

At M.P. vapor pressure is 0.23 mm.

X-Ray Crystallographic Data:

System	Space Group	a	Atoms/Unit Cell
cubic	$O_h$	5.333	2

Hygroscopicity: Reacts with water to form KOH and  $H_2$ .

Caution: Keep under liquid containing no oxygen; e.g., petroleum or in an inert atmosphere of argon or nitrogen.

Solubility Data: Soluble in liquid  $NH_3$ , ethylene diamine, aniline, and mercury.

Reacts with water, and alcohol.

Health Hazard: Extremely caustic to all tissues. The fumes of potassium oxide are very toxic.

Safety Classifications:

OSM: Class 2

ICC: Listed under "Explosives and Other Dangerous Materials" as a "Flammable Solid"; yellow label.

Fire and Explosion Hazard: Potassium reacts vigorously with water to form caustic KOH and evolve hydrogen. The heat evolved causes the potassium to melt and the hydrogen to burn. If there is any confinement, the hydrogen may explode. Burning potassium is difficult to extinguish. To fight a fire, use dry powdered soda ash, graphite, or special mixtures of dry chemicals. Even when stored under mineral oil, the peroxide ( $K_2O_2$ ) and superoxide ( $KO_2$  or  $K_2O_4$ ) may form, and an explosion may occur when the material is handled or cut. Potassium which has become coated with a layer of oxide should be burned. The fumes of potassium oxide are highly toxic. Do not use  $CCl_4$  on fire as an explosion may result. Use powdered talc.

Electrostatic Sensitivity: —

Use in Pyrotechnics: As a fuel and to color burning smoke compositions violet.

Additional Reference:

- 1) C.A. 37, 2578 (1943)

# POTASSIUM BICARBONATE

(Potassium Acid Carbonate,  
Potassium Hydrogen Carbonate)

Refs.

Formula:	KHCO <sub>3</sub>	
Specification No.:	MIL-P-3173	
Molecular Weight:	100.11	
Crystalline Form:	monoclinic	1
Color:	colorless	1
Density, g./ml.:	(solid) 2.17	1
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	-229.3	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	-205.7	86
Entropy:	—	
Melting Point:	—	
Heat of Fusion:	—	
Boiling Point:	—	
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature, °C:	100-200	1
Decomposition Products:	K <sub>2</sub> CO <sub>3</sub> + CO <sub>2</sub> + H <sub>2</sub> O	44V22 II
Heat of Dissociation, cal./mole:	15,730	Addnl. Refs. 1, 2
Vapor Pressure of Dissociation (to CO <sub>2</sub> + H <sub>2</sub> O) is given by		Addnl. Ref. 1
$\log P_{mm} = 10.832 - \frac{3420}{T_{abs.}}$		
$2KHCO_3(s) = K_2CO_3(s) + CO_2(g) + H_2O(g)$		
Press. atm.	.0054 .1463 .2527 .6203 .8034 .9645	91
Temp. °K	340.8 389.5 400.3 419.4 424.9 429.1	
X-Ray Crystallographic Data:		
Space Group	a b c Axial Angle Molecules/Unit Cell	18V4
C <sub>2h</sub>	15.176 5.630 3.708 β = 103° 45'	4
Hygroscopicity: Nonhygroscopic. Stable in dry air. In more than 70% saturated humidity it absorbs water. In damp air loses CO <sub>2</sub> and forms a coating of K <sub>2</sub> CO <sub>3</sub> .		44V22 II
Solubility Data: In cold water:		1
In water at 60°C:		
In alcohol:		insoluble
Health Hazard: Excessive doses may cause hyperkalemia or alkalosis.		29

**Potassium Bicarbonate (page 2)**

**Safety Classifications:**

OSM:	not listed
ICC:	not listed

**Fire and Explosion Hazard:**

---

**Electrostatic Sensitivity:**

---

**Use in Pyrotechnics:** As a retardant, and to color burning compositions purplish-red.

**Additional References:**

- 1) "The Dissociation Pressures of the Alkali Carbonates. Part II. Potassium, Rubidium, and Cesium Hydrogen Carbonates," R. M. Caven and H. J. Sand, *J. Chem. Soc.* 105, 2752 (1914)

### Refs.

**MIL-P-150A**

iii

1

1

44V22 I

## 1.9

## 1.9

### 3.9

1

65

**1, 20**

42. 44V22 I

9

65

**20. 29**

**20, 29**

**Addn'l. Ref. 1**

65

**Potassium Chlorate, KClO<sub>3</sub> (page 2)**

Vapor Pressure: —

X-Ray Crystallographic Data:

System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell
monoclinic	C <sub>2h</sub>	4.647	5.585	7.085	$\beta = 109^\circ 38'$	2
	°C	a	b	c		
	20	4.647	5.585	7.085		
	90	4.565	5.600	7.122		
	150	4.679	5.611	7.152		
	200	4.692	5.621	7.180		
	250	4.706	5.632	7.209		

Hygroscopicity: R.T., after equilibrium has been established in a vacuum desiccator:

R.H.%	65	75	86	93
Time Exposed	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.
Gain mg./g.				
R <sup>1</sup>	0.1	0.1	0.1	0.2
S <sup>1</sup>	—	<.1	0.2	—

R<sup>1</sup> = reagent grade; S<sup>1</sup> = spec. grade

Critical R.H.:

Reagent grade, 97.7% at 25°C

Spec. grade, 97.9% at 26.2°C

Water absorbed by 2.000 g. at 25°C (C.P. material):

Fineness	Hours	g. H <sub>2</sub> O absorbed
40-80 mesh	45¼	0.0650
	69¾	0.1056
	93½	0.1392
	122¼	0.2340
ground	16	0.0248
very fine	69	0.1062
	88¾	0.1488

Solubility Data: In water at 20°C: 7.1 g./100 ml.  
at 100°C: 57 g./100 ml.  
In alkalis: slightly soluble

At 25°C, g./100 g. solvent:

In ethyl alcohol: 0.81  
In glycerol: 1.05  
In acetone: insoluble  
In ethylene glycol: 1.21  
At 20°C in methyl alcohol: 0.095



**Potassium Chlorate,  $\text{KClO}_3$  (page 3)**

**Health Hazard:** Slight to moderately poisonous. The principal toxic effects of chlorates are the production of methemoglobin and the destruction of red blood corpuscles. Chlorates are also irritating to the genito-urinary tract and to the kidneys. The probable lethal human dose is 50-500 mg./kg.

12, 25, 26,  
29, 65, 93

**Safety Classifications:**

**OSM:** Class 1. Class 2 when not packed or stored in original containers or equivalent.

**ICC:** Listed under "Explosives and Other Dangerous Articles" and classed as oxydizing material: yellow label.

**Fire and Explosion Hazard:** Potassium chlorate is exploded by shock, or heat, and when rubbed in the presence of organic or reducing material (sugar, charcoal, shellac, sulfur, starch, sawdust,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4$  compounds, cyanides, phosphorus or antimony sulphide).  $\text{KClO}_3$  is sensitive to friction. Chlorate fires should be fought with large streams of water or with water fog. *Note.* See references for important precautions in the handling of potassium chlorate alone and with mixtures. The danger of spontaneous combustion with sulfur is greatly reduced by the addition of potassium bicarbonate.

12, 29, 14

**Explosive Tests on Specification Grade Potassium Chlorate:**

**Explosion Temp. Test (5 sec. value),  $^{\circ}\text{C}$ :** 467

**Impact Test Values: (10% point)**

**P.A. Apparatus, 2 kg. hammer**

(22 mg. charge) ; in :

40 +

**B.M. Apparatus, 2 kg. hammer, cm :**

100 +

19

33

33

33

**Use in Pyrotechnics:** As an oxidizer and to impart a purple-red color to burning compositions.

1, 16, 17

**Additional References:**

- 1) "The Formation and Decomposition of Potassium Perchlorate and a New Determination of the Heat of Decomposition," C.A. 27, 1264 (1933)
- 2) "Refinement of the Crystal Structure of Sodium Chlorate and Potassium Chlorate," J. G. Bower et al., Univ. of California, AFOSR Number TN-59-104, ASTIA Document Number AD 210, 386 (1959)
- 3) "Hygroscopic Properties of Sodium, Potassium and Ammonium Nitrates, Potassium Chlorate and Mercury Fulminate," G. B. Taylor and W. C. Cope, Met. & Chem. Eng. 15, 141 (1916)
- 4) G. Ramachandran and M. Lonappan, Acta. Cryst. 10, 281 (1957)

**POTASSIUM NITRATE, KNO<sub>3</sub>**  
(Saltpeter, Niter)

*Refs.*  
1, 29

Percent Oxygen:	47.48	
Specification No.:	MIL-P-156B	
The spec. covers three classes of about equal purity but of different granulation. Class 2 is used in pyrotechnics.		
Molecular Weight:	101.10	
Crystalline Form:	rhombic or trigonal	1
Color:	colorless	1
Density, g./ml.: (solid) 2.109; (liquid) $2.123 - .755 \times 10^{-4}t^{\circ}\text{C}$ (over the range 350–565°C)		1 40V2
Coefficient of Thermal Expansion, cubical, 0–100°C: $1967 \times 10^{-7}$ See also Ref. 54V2		1
Heat of Formation, Kcal./mole at 298°K:	–117.76	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	–93.96	1, 9
Entropy, cal./deg./mole at 298°K: See table below	31.81	3
Melting Point:	611°K (338°C)	7
Heat of Fusion, cal./mole:	2800	4
Boiling Point:	decomposes at 673°K (400°C)	1
Transition Point:	$\alpha$ to $\beta$ at 401°K (128°C)	4
Heat of Transition, cal./mole:	1400	4
Heat of Sublimation:	—	

**HEAT CONTENT AND ENTROPY OF KNO<sub>3</sub> (c, l)**  
(Base,  $\alpha$ -crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350 . . . . .	1230	3.80	600 . . . . .	3630	22.36
400 . . . . .	2450	7.17	611 ( $\beta$ ) . . .	9970	22.87
401 ( $\alpha$ ) . . .	2520	7.24	611 (l) . . .	12,770	27.45
401 ( $\beta$ ) . . .	3920	10.73	700 . . . . .	15,400	31.46
500 . . . . .	6780	17.11			

KNO<sub>3</sub> ( $\alpha$ ):  
Enthalpy:  $H_T - H_{298.15} = 14.55T + 14.20 \times 10^{-4}T^2 - 5600$  (0.1 percent; 298–401°K)  
Heat Capacity:  $C_p = 14.55 + 28.40 \times 10^{-4}T$

KNO<sub>3</sub> ( $\beta$ ):  
Enthalpy:  $H_T - H_{298.15} = 28.80T - 7625$  (0.1 percent; 401–611°K)

KNO<sub>3</sub> (l):  
Enthalpy:  $H_T - H_{298.15} = 23.50T - 5250$  (0.1 percent; 611–700°K)

**Potassium Nitrate, KNO<sub>3</sub> (page 2)**

Heat Capacity, cal./deg./mole: (solid)  $\alpha = 28.01$  (liquid) 29.50 4, 5  
 $\beta = 28.8$

See table above

Decomposition Temperature, °C: 400 1

Decomposition Products: From 650 to 750°C. The products of decomposition are KNO<sub>2</sub> + O + traces of NO<sub>2</sub>. At 800°C decomposition is more extensive with KNO<sub>3</sub> decomposing to form K<sub>2</sub>O, N, and O. 35

For DTA and TGA see Refs. 33 and 47

Vapor Pressure: —

X-Ray Crystallographic Data:

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell</i>	1
hexagonal	C <sub>3v</sub>	4.365	$\alpha = 76^\circ 56'$	1	

Hygroscopicity: Gain in mg./g. at R.T. after equilibrium has been established in vacuum dessicators. 32

% R.H.	65	75	86	93
Time	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.	24 hrs. equil.
Spec. grade	— <1	— 0.2	— —	55.2 —
Purified	— —	— —	— <.1	— <.1

Critical R.H.: Specification grade, 91.7% at 20.0°C 32  
Purified material, 91.8% at 26.2°C

Water absorbed by 2.0000 g. at 25°C (C.P. material):

Fineness	Hrs.	H <sub>2</sub> O absorbed, g.
40-80 mesh	2¾	0.0147
	18¾	0.1136
	25¼	0.1527
	42¾	0.2687
	47	0.2896
ground	7¼	0.0453
very	16¼	0.1056
fine	40¼	0.2580

Specification Grade, gain % at 70°F and 90% R.H.: 0.76 33

Solubility Data: In water (g.100/ml.): 13.3 at 0°C, 31.6 at 20°C, and 247 at 100°C 1

In alcohol and ether: insoluble

Health Hazard: Ingestion of large amounts may cause violent irritation of the intestinal lining. Prolonged exposure to small amounts may result in anemia and nephritis. Moderately poisonous on ingestion or inhalation. 12, 29, 93

**Potassium Nitrate, KNO<sub>3</sub> (page 3)**

**Safety Classifications:**

OSM: Class 1. Class 2 when not packed or stored in original shipping containers.

ICC: Listed under "Explosives and Other Dangerous Articles" as oxidizing material; yellow label.

**Fire and Explosion Hazard:** Dangerous, as it is a fire and explosion hazard. As an oxidizer it can give up its oxygen to other materials to produce a vigorous reaction which may result in detonation. Toxic fumes are emitted on decomposition. 12, 14

Potassium nitrate is a strong oxidizer, sensitive to shock, and can be easily detonated. When mixed with flammable materials it becomes very sensitive.

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:** As an oxidizer and to impart a purple-red color to burning compositions. 17

**Additional References:**

- 1) "The Kinetics of Thermal Decomposition of Potassium Nitrate and of the Reaction between Potassium Nitrate and Oxygen," E. Freeman, J. Am. Chem. Soc. 79, 838 (1957)
- 2) "Simple Method for Derivative Thermal Analysis," E. Freeman and D. Edelman, Anal. Chem. 31, 624 (1959)
- 3) "Instrumentation and Applications to Thermogravimetry and Differential Thermal Analysis," C. Campbell et al., Anal. Chem. 31, 1189 (1959)
- 4) "A Thermoanalytical Study of the Ignition and Combustion Reactions of Black Powder," C. Campbell and G. Weingarten, Trans. Faraday Soc. 55, No. 444, 2221 (1959)
- 5) "Hygroscopic Properties of Sodium, Potassium and Ammonium Nitrates, Potassium Chlorate and Mercury Fulminate," G. B. Taylor and W. C. Cope, Met. & Chem. Eng. 15, 141 (1916)

**POTASSIUM OXIDE, K<sub>2</sub>O**  
(Potassium Monoxide)

Refs.

Specification No.:	—	1
Molecular Weight:	94.20	
Crystalline Form:	cubic	1
Color:	colorless to grey	1, 44V22I
White at ordinary temp., yellow when hot.		
Density, g./ml.:	(solid) 2.32°	1
Coefficient of Thermal Expansion:	—	
Heat of Formation, cal./mole at 298°K:	-86,400 (± 2000)	2
See table below		
Free Energy of Formation, cal./mole at 298°K:	-76,300 (± 2800)	2
See table below		
Free Energy Equations:		
Reaction	Range of Validity, °K	2
1) 2K (c) + ½ O <sub>2</sub> (g) = K <sub>2</sub> O (c)	298.16-336.4	
Δ F <sub>T</sub> <sup>o</sup> = -86,400 + 33.90T		
2) 2K (l) + ½ O <sub>2</sub> (g) = K <sub>2</sub> O (c)	336.4-1049	
Δ F <sub>T</sub> <sup>o</sup> = -87,380 + 1.15T log T + 33.90T		
3) 2K (g) + ½ O <sub>2</sub> (g) = K <sub>2</sub> O (c)	1049-1500	
Δ F <sub>T</sub> <sup>o</sup> = -103,090 - 16.12T log T + 129.64T		

**HEAT AND FREE ENERGY OF FORMATION OF K<sub>2</sub>O (c)**

T, °K	Δ H (cal./mole)	Δ F <sup>o</sup> (cal./mole)
298.16 . . . .	-86,400 (± 2000)	-76,300 (± 2800)
336.4 . . . .	-86,400	-75,000
336.4 . . . .	-87,600	-75,000
400 . . . . .	-87,600	-72,600
500 . . . . .	-87,600	-68,000
600 . . . . .	-87,700	-65,100
700 . . . . .	-87,700	-61,400
800 . . . . .	-87,800	-57,600
900 . . . . .	-87,800	-53,800
1000 . . . . .	-87,900	-50,000
1049 . . . . .	-87,900	-48,200
1049 . . . . .	-125,800	-48,200
1100 . . . . .	-125,400	-44,400
1200 . . . . .	-124,700	-37,100
1300 . . . . .	-124,000	-29,800
1400 . . . . .	-123,300	-22,600
1500 . . . . .	-122,600	-15,400

Phase changes of Metal

M.P., 336.4°K; Δ H = 558 cal./g.-atom  
B.P., 1049°K; Δ H = 18,925 cal./g.-atom

**Potassium Oxide, K<sub>2</sub>O (page 2)**

Entropy, cal./deg./mole at 298°K:	23.5 ± 2.5	24			
Melting Point:	—				
Heat of Fusion:	not obtainable	7			
Boiling Point:	—				
Transition Point:	1253°K (980°C)	6			
Heat of Transition, Kcal./mole:	6.8	6			
Heat of Sublimation:	—				
Heat Content or Enthalpy:	—				
Heat Capacity:	—				
Decomposition Temperature:	below 763°K at 1750 ± 100°K	8 7			
Decomposition Products:	—				
Vapor Pressure of alkali oxide and alkali metal in equil. with solid alkali oxide, atm. at 1000°K (calcd.):	10 <sup>-18</sup>	Addnl. Ref. 5			
X-Ray Crystallographic Data:					
System	Space Group	a	Molecules/Cubic Cell	18	
cubic		6.436			
Hygroscopicity:	Reacts with water to form KOH with evolution of considerable heat.				
Solubility Data:	Very soluble in water and is slightly soluble in alcohol and ether.				
The heat of solution in water, Kcal./mole:	75			44V22 I	
Health Hazard:	Has a caustic reaction on the skin and respiratory system.				12, 25, 29
	Because it causes dermatitis, avoid its dust and treat exposed skin with large quantities of water.				
Safety Classifications:					
OSM:	not listed				
ICC:	not listed				
	Caustic potash liquid is classified under "Explosives and Other Dangerous Articles" as a corrosive liquid.				
Fire and Explosion Hazard:	Considerable heat is developed by reaction with water. Highly caustic.				12
Electrostatic Sensitivity:	—				
Use in Pyrotechnics:	a product of burning potassium compounds				

**Additional References:**

- 1) "Stability of Solid and Gaseous Alkali and Alkaline Earth Oxides," L. Brewer and D. F. Mastick, J. Am. Chem. Soc. 73, 2045 (1951)

**POTASSIUM PERCHLORATE, KClO<sub>4</sub>**  
(Potassium Hyperchlorate)

Percent Oxygen:	46.19		
Specification No.:	JAN-P-217(2)		
The spec. covers one grade and four granulations.			
Molecular Weight:	138.55		
Crystalline Form:	rhombic	1	
Color:	colorless	1	
Density, g./ml.:	(solid) 2.52	1	
Coefficient of Thermal Expansion, cubical, from -78° to + 18°C:	$14 \times 10^{-6}$	44V22 I	
Heat of Formation, Kcal./mole at 298°K:	-103.6	1, 9	
Free Energy of Formation, Kcal./mole at 298°K:	-72.7	1, 9	
Entropy, cal./deg./mole at 298°K:	36.1	1, 3, 9	
Melting Point:	337°K (610 ± 10°C)	1	
Literature values vary from < 400° to 610°C, with and without mention of decomposition.		65	
Heat of Fusion:	—		
Boiling Point:	decomposes at 926°K (653°C)	Addnl. Ref. 7	
Transition Point:	$\alpha$ (rhombic) to $\beta$ (cubic) at 572°K (299°C)	9	
Heat of Transition, Kcal./mole:	3.29	9	
Heat of Sublimation:	—		
Heat Content or Enthalpy:	—		
Heat Capacity, cal./deg./mole:	(solid) 26.33	4, 9 Addnl. Ref. 4	
Decomposition Temperature, °C: Starts at about 530° and is complex. See Addnl. Ref. 10 for TGA		47	
Heat of Decomposition of Perchlorates, Kg. cal./mole (constant volume) at room temperature, $\text{KClO}_4 \rightarrow \text{KClO}_2 + \text{O}_2$ :		Addnl. Ref. 8	
	1.73		
Decomposition Products:	KCl + 4O	20	
Vapor Pressure:			
See 54V1			
X-Ray Crystallographic Data:			
System	Space Group	a b c Molecular/ Unit Cell	
rhombic	$V_{16}^s$	8.834 5.650 7.240 4	
cubic (340°C)	$T_{24}^s$ or $T_{24}^s$	7.47	Addnl. Ref. 9 97V6
	$D_{2h}^{16}$	8.857 5.653 7.254 4	

**Potassium Perchlorate, KClO<sub>4</sub> (page 2)**

Hygroscopicity: Gain (mg./g.) at 23-5°C and 93% R.H. after equilibrium has been established in a vacuum desiccator.		32
Spec. grade, after 24 hrs.:	1	
Purified, at equilibrium:	<1.0	
Critical R.H. of spec. grade material:	99.3% at 26.2°C	32
Solubility Data: In water, g./100 ml.:	0.75 at 0°C and 21.8 at 100°C	1, 65
Solubility in Nonaqueous Solvents at 25°C:		
Solvent	g./100 g. of solvent	65
Acetone	0.155	72
Eethyl acetate	0.0015	77
Ethyl alcohol	0.012	
Ethyl ether	insoluble	
Methyl alcohol	0.105	
Ethyl glycol	1.03	
Health Hazard: Moderately toxic and irritating to the skin, mucous membranes, and respiratory tract. It may affect the kidneys. Avoid contact with KClO <sub>4</sub> . The probable lethal dose for humans is 50-500 mg./kg.		93, 12, 29, 65
Safety Classifications:		
OSM: Class 1. Class 2 when not packed in original shipping containers or equivalent.		
ICC: Listed under Explosives and Other Dangerous Materials. Classed as oxidizing material; yellow label.		
Fire and Explosion Hazard: A fire and explosive hazard, particularly when mixed with organic material, finely divided metals or sulfur. When heated it emits highly toxic fumes. For fighting a fire or potassium perchlorate alone use water.		12, 14
Electrostatic Sensitivity:	—	
Impact Tests: Charge weight = 0.023 g.		33
Bureau of Mines Apparatus, 2 kg. wt., cm.:	(10% point) 100 +	
P.A. Apparatus, 2 kg. wt., in.:	(10% point) 40 +	
Use in Pyrotechnics: As an oxidizer and to color burning compositions purple-red.		
Additional References:		
1) Ref. 47		
2) "Simple Method for Derivative Differential Analysis," E. Freeman and D. Edelman, Anal. Chem. 31, 624 (1959)		
3) M. M. Markowitz, J. Phys. Chem. 61, 505 (1957)		
4) L. L. Bircumshaw and B. H. Newman, Proc. Royal Society (London) A227, 115 (1954)		
5) A. F. Harvey et al., J. Am. Chem. Soc. 76, 3270 (1954)		



Potassium Perchlorate,  $\text{KClO}_4$  (page 3)

- 6) "Precise Studies of the Crystal Structures of Lithium Perchlorate Trihydrate, Anhydrous Lithium Perchlorate, and Potassium Perchlorate," R. J. Prosen and K. N. Trueblood, Perchlorates TN-2, OSRTN 56-563, ASTIA Document No. AD 110-384 (1956)
- 7) C. Duval, C.A. 42, 8698 (1948)
- 8) K. A. Hoffman and P. H. Marin, C.A. 27, 1264 (1933)
- 9) "The Crystal Structure of Potassium Perchlorate— $\text{KClO}_4$ ," N. V. Mani, Proceedings of the Indian Academy of Science, pp. 143-151 (1957)
- 10) Anal. Chem. Acta 2, 105 (1948)

## SHELLAC

(For trade names and manufacturers, see Ref. 60)

Refs.

Shellac is a variable natural product obtained from various species of *Acacia*.

Shellac is the only resinous substance of animal origin. It is produced by an insect (*Tachadia lacca*) which lives on certain trees of southern Asia. The insect takes up sap through its stinger and after a semi-polymerization process exudes it as a gum. This lac secretion coats their bodies and the twigs of the trees with a heavy incrustation which is scraped off and forms the commercial stick lac. This contains not only the lac resin but also woody matter, lac dye, and the bodies of insects. The seed lac is ground and washed to remove the wood and most of the coloring matter. Shellac is prepared from the seed lac by melting or by extraction with solvents. The molten material is spread over a hot cylinder, stretched, and cooled. The cooled sheet is then broken into flakes of shellac. After purification, shellac varies in color from orange to lemon yellow. Orange shellac may contain as much as 1% of powdered orpiment ( $As_2O_3$ ).

15, 20, 59,  
52V7

Chemically, shellac contains condensed long chain esters of condensed polyhydroxy acids together with rosin and wax. By solvent action the wax content of the seed lac is reduced to 1%. Shellac is graded by color and amount of dirt. The best grade contains no resin, but in inferior grades the resin content may be as high as 12%.

### Characteristics of Shellac (analytical):

Acid Number:	48-64	1
Ester Number:	137-63	1
Saponification Number:	194-213	1
Iodine Number:	185-210	29

Specification No.: MIL-S-20526

(Includes U.S. Army Specification No. 50-11-17A)

The spec. covers three grades which differ in purity. Grade A is used in both primer pyrotechnic compositions. Grade A includes the grades of orange shellac known as "Double Triangle G," "Diamond I," "Superfine," the highest grades, "D.C." and "V.S.O." The so-called machine-made shellacs, such as "CV" and "CVTN," in general fall under Grade A.

Molecular Weight:	—	
Crystalline Form:	—	
Color:	pale orange to lemon yellow	59
Density, g./ml.:	(solid) 1.08-1.13	1
Coefficient of Thermal Expansion:	—	
Heat of Formation:	—	
Free Energy:	—	
Entropy:	—	
Melting Point:	indefinite 388-393°K (115-120°C)	20, 9
Heat of Fusion:	—	
Boiling Point:	decomposes	

# Shellac (page 2)

Transition Point:	_____	
Heat of Sublimation:	_____	
Heat Content or Enthalpy:	_____	
Heat Capacity:	_____	
Decomposition Temperature:	_____	
Decomposition Products:	_____	
Vapor Pressure:	_____	
X-Ray Crystallographic Data:	_____	
Hygroscopicity: Nonhygroscopic and not altered on exposure to the air.		1
Solubility Data, g./100 g. solution:		29
In water:	insoluble	
In alcohol:	85-90 (very slowly soluble)	
In ether:	13-15	
In benzene:	10-20	
Sparingly soluble in oil or turpentine. Soluble in aqueous ethanolamines, alkalis, or borax. Solubility in petroleum ether, 2-6 g./100 g. solution. Soluble in the lower aliphatic alcohols but not in hydrocarbons.		29, 59
Health Hazard:	none	
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard: Easily ignited and continues to burn.		60
Ignition Temp. of Dust Cloud, °C:	390	26
Minimum Explosive Concentration of Dust, mg./l.:	15	26
Electrostatic Sensitivity, minimum energy required for ignition of dust cloud by electric sparks (millijoules) :	10	26
Use in Pyrotechnics: As a binder, a fuel retardant, and to reduce absorption of moisture. It is applied as an alcoholic solution. The alcohol is allowed to evaporate after application.		20V1, 20V3

# SILICON, Si

Refs.

Specification No.:	JAN-S-230 and Amendment 1	
Amendment 1 lists two grades differing slightly in purity, and four classes differing in granulation.		
Molecular Weight:	28.05	
Crystalline Form:	Needle-like crystals or octahedral platelets (cubic). Occurs in three forms; adamantine (cubic), amorphous, and graphitoidal.	1, 29
Color:	Lustrous black to gray. The amorphous form is a dark brown powder, steel grey, black plates.	1, 29
Types and Differences of Behavior:	Brown amorphous silicon dissolves in molten metals and burns in air to form SiO <sub>2</sub> . Black, shiny graphitoidal silicon is not easily oxidized and not attacked by the common acids, but is soluble in alkalis. Crystalline silicon is obtained in dark, steel-grey globules or six-sided pyramids. It is less reactive than the amorphous form, but is attacked by boiling water. The three forms are obtained by reduction. Commercial silicon is the graphitoidal flake form and when refined contains 97% Si and less than 1% iron.	16, 29
Density, g./ml.:	(solid) adamantine, 2.42 amorphous, 2.00 graphitoidal, about 2.4	1
Coefficient of Thermal Expansion, linear at 25°C:	$4.2 \times 10^{-6}$	29
40°C:	$7.63 \times 10^{-6}$	1
Heat of Formation, Kcal./mole at 298°K:	(gas) 880.4	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 77.41	1, 9
Entropy, cal./deg./mole at 298°K:	(gas) 40.12 (c) 4.53	1, 5, 9 1, 5, 9
See Table a		
Melting Point:	1655°K (1412°C)	4
Heat of Fusion, cal./mole:	12,100	4
Boiling Point:	2950°K (2677°C)	5
Heat of Vaporization, Kcal./mole:	about 72.6	40V2
Transition Point:	none up to 1273°K (1000°C) about 2873°K (2600°C)	Addnl. Ref. 1 40
Heat of Sublimation, Kcal./mole:	(monatomic Si) 105	5
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 769	

a. HEAT CONTENT AND ENTROPY OF Si (c, l)  
(Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	515	1.48	1400 . . . . .	6680	9.04
500 . . . . .	1060	2.69	1500 . . . . .	7340	9.49
600 . . . . .	1630	3.73	1600 . . . . .	8010	9.92
700 . . . . .	2220	4.64	1685 (c) . . .	8580	10.27
800 . . . . .	2830	5.46	1685 (l) . . .	20,680	17.45
900 . . . . .	3450	6.19	1700 . . . . .	20,770	17.50
1000 . . . . .	4080	6.85	1800 . . . . .	21,380	17.85
1100 . . . . .	4720	7.46	1900 . . . . .	21,990	18.18
1200 . . . . .	5360	8.02	2000 . . . . .	22,600	18.49
1300 . . . . .	6020	8.55			

## Si (c) :

Enthalpy:  $H_T - H_{298.15} = 5.70T + 0.35 \times 10^{-3}T^2 + 1.04 \times 10^5 T^{-1} - 2079$   
(0.3 percent; 298-1685°K)

Heat Capacity:  $C_p = 5.70 + 0.70 \times 10^{-3}T - 1.04 \times 10^5 T^{-2}$

## Si (l) :

Enthalpy:  $H_T - H_{298.15} = 6.10T + 10,400$  (0.1 percent; 1685-2000°K)

Heat Capacity:  $C_p = 6.10$

b. HEAT CONTENT AND ENTROPY OF Si (g)  
(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	535	1.54	1900 . . . . .	8140	9.43
500 . . . . .	1045	2.68	2000 . . . . .	8665	9.70
600 . . . . .	1555	3.61	2200 . . . . .	9715	10.20
700 . . . . .	2060	4.39	2400 . . . . .	10,780	10.67
800 . . . . .	2560	5.06	2600 . . . . .	11,850	11.10
900 . . . . .	3060	5.65	2800 . . . . .	12,935	11.50
1000 . . . . .	3565	6.18	3000 . . . . .	14,020	11.87
1100 . . . . .	4065	6.66	3500 . . . . .	16,765	12.71
1200 . . . . .	4565	7.09	4000 . . . . .	19,520	13.45
1300 . . . . .	5070	7.49	4500 . . . . .	22,280	14.10
1400 . . . . .	5575	7.87	5000 . . . . .	25,040	14.69
1500 . . . . .	6085	8.22	6000 . . . . .	30,555	15.69
1600 . . . . .	6595	8.55	7000 . . . . .	36,105	16.55
1700 . . . . .	7105	8.86	8000 . . . . .	41,845	17.31
1800 . . . . .	7625	9.15			

Silicon, Si (page 3)

Si (g) :

Enthalpy:  $H_T - H_{298.15} = 4.82T + 0.09 \times 10^{-3}T^2 - 0.42 \times 10^{-5}T^3 - 1304$   
(0.3 percent; 298-5000°K)

Heat Capacity:  $C_p = 4.82 + 0.18 \times 10^{-3}T + 0.42 \times 10^{-5}T^2$

Heat Capacity, cal./deg./mole at 298°K: (solid) 4.80  
(liquid) 7.0  
(gas) 5.32

Also see above

Decomposition Temperature: \_\_\_\_\_

Decomposition Products: \_\_\_\_\_

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	1724	1888	2000	2083	2220	2297	1420

at melting point, mm.

0.075

X-Ray Crystallographic Data:

System	Space Group	a	Atoms/Unit Cell
cubic	$O_h$	5.4173	8

Hygroscopicity (milled Si), cumulative increase in weight after:  
storage over H<sub>2</sub>O for 18 days 4.5% 3 days in oven at 105°C 0.4%

(Some caking of powder noted.)

Solubility data:

In water: insoluble

In molten alkali oxide, HF: soluble

Health Hazard: slight

Safety Classifications:

OSM: Class 2  
ICC: not listed. Probably classed as a flammable solid  
U.N.: inflammable solid

Fire and Explosion Hazard: Powdered silicon when heated in the air is a dangerous fire hazard. It burns with intense heat and reacts explosively with oxidizing materials, and with water or steam. Prevent water from contacting the material. Store and process only in a room or building adequately vented at the highest point to prevent accumulation of hydrogen gas which results from the reaction of powdered metal and moisture. In the repair or maintenance of buildings or equipment, powder or dust should be removed and nonsparking tools used.

The powder is moderately explosive.

Electrostatic Sensitivity, minimum energy required for ignition of powder by electric sparks, millijoules for dust cloud: 80

Ignition Temperature, °C: (dust cloud) 775  
(dust layer) 950

Minimum Explosive Concentration of powdered silicon, mg./l: 100

Use in Pyrotechnics: as a fuel

Additional References:

1) J. Phys. Chem. 60, 509 (1956)

SILICON DIOXIDE, SiO <sub>2</sub>				Refs.
(Quartz, Silica, Silicic Anhydride, Rock Crystal, Cristobalite)				1, 12
Percent Oxygen:	53.25			
Specification No.:	-----			
Molecular Weight:	60.06			
Crystalline Form:				1
Type of SiO <sub>2</sub>	Crystalline Form	Density	M.P. °C	
cristobalite	cubic or tetragonal	2.32	1710	
lechatelierite		2.20		
quartz	hexagonal	2.653-2.660	<1470	
tridymite	rhombic	2.28-2.33	1670	
Color:	colorless			1
Density, g./ml.:	(solid) 2.653-2.660			1
See table above				
Coefficient of Thermal Expansion:				1
quartz (c), -190° to + 16°C:	5.21 × 10 <sup>-6</sup>			
parallel to axis, 0-80°C:	7.97 × 10 <sup>-6</sup>			
perpendicular to axis, 0-80°C:	13.37 × 10 <sup>-6</sup>			
fused, -191° to + 16°C:	0.256 × 10 <sup>-6</sup>			
0-30°C:	0.42 × 10 <sup>-6</sup>			
0-100°C:	0.50 × 10 <sup>-6</sup>			
0-800°C:	0.546 × 10 <sup>-6</sup>			
0-1200°C:	0.585 × 10 <sup>-6</sup>			
cubic expansion, quartz, 50-60°C:	0.3530 × 10 <sup>-4</sup>			
Heat of Formation, Kcal./mole at 298°K:	quartz, -205.4			1, 9
	cristobalite, -205.0			1
Free Energy of Formation, Kcal./mole at 298°K:	quartz, -192.4			1
	cristobalite, -192.1			
	tridymite, -191.9			
a. HEAT AND FREE ENERGY OF FORMATION OF SiO <sub>2</sub> (α-quartz, β-quartz, l)				2
T, °K	Δ H (cal./mole)	Δ F° (cal./mole)		
298.16 . . .	-209,900 (± 1000)	-192,500 (± 1000)		
400 . . . . .	-209,900	-192,500		
500 . . . . .	-209,800	-188,500		
600 . . . . .	-209,700	-183,800		
700 . . . . .	-209,500	-179,500		
800 . . . . .	-209,200	-175,200		
848 . . . . .	-209,000	-173,200		
848 . . . . .	-208,700	-173,200		
900 . . . . .	-208,600	-171,000		
1000 . . . . .	-208,400	-166,800		
1100 . . . . .	-208,300	-162,700		
1200 . . . . .	-208,100	-158,500		
1300 . . . . .	-207,900	-154,400		

Silicon Dioxide, SiO<sub>2</sub> (page 2)

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
1400 . . . . .	-207,800	-150,300
1500 . . . . .	-207,600	-146,200
1600 . . . . .	-207,400	-142,100
1683 . . . . .	-207,300	-138,700
1683 . . . . .	-218,400	-138,700
1700 . . . . .	-218,300	-138,000
1800 . . . . .	-218,200	-133,200
1883 . . . . .	-218,100	-129,300
1883 . . . . .	-216,000	-129,300
1900 . . . . .	-215,900	-128,500
2000 . . . . .	-215,200	-123,900

Phase changes of Oxide

T.P. (α-quartz to β-quartz), 848°K; Δ H = 290 cal./mole

T.P. (β-quartz to β-tridymite), 1140°K; Δ H = 180 cal./mole

M.P., 1883°K; Δ H = 2040 cal./mole

b. HEAT AND FREE ENERGY OF FORMATION OF SiO<sub>2</sub>  
(α-cristobalite; β-cristobalite)

2

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16 . . . . .	-209,550 (± 250)	-196,650 (± 300)
400 . . . . .	-209,600	-192,200
500 . . . . .	-209,500	-187,900
523 . . . . .	-209,450	-186,900
523 . . . . .	-209,250	-186,900
600 . . . . .	-209,100	-183,600
700 . . . . .	-208,900	-179,350
800 . . . . .	-208,700	-175,150
900 . . . . .	-208,500	-171,000
1000 . . . . .	-208,300	-166,800
1100 . . . . .	-208,100	-162,700
1200 . . . . .	-207,950	-158,550
1300 . . . . .	-207,750	-154,450
1400 . . . . .	-207,550	-150,350
1500 . . . . .	-207,350	-146,300
1600 . . . . .	-207,200	-142,200
1683 . . . . .	-207,050	-138,850
1683 . . . . .	-218,150	-138,850
1700 . . . . .	-218,100	-138,050
1800 . . . . .	-218,000	-133,350
1900 . . . . .	-217,850	-128,650
2000 . . . . .	-217,700	-123,950

Phase changes of Oxide

T.P., 523°K; Δ H = 200 cal./mole



c. HEAT AND FREE ENERGY OF FORMATION OF SiO<sub>2</sub>  
( $\alpha$ -trid.,  $\beta$ -trid., l)

T, °K	$\Delta H$ (cal./mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . .	-209,400 ( $\pm$ 1060)	-196,500 ( $\pm$ 1000)
390 . . . . .	-209,400	-192,630
390 . . . . .	-209,400	-192,600
400 . . . . .	-209,400	-192,100
500 . . . . .	-209,200	-187,800
600 . . . . .	-209,100	-183,600
700 . . . . .	-208,900	-179,100
800 . . . . .	-208,700	-175,200
900 . . . . .	-208,500	-171,000
1000 . . . . .	-208,300	-166,800
1100 . . . . .	-208,100	-162,700
1200 . . . . .	-207,900	-158,600
1300 . . . . .	-207,700	-154,400
1400 . . . . .	-207,500	-150,100
1500 . . . . .	-207,300	-146,300
1600 . . . . .	-207,200	-142,200
1683 . . . . .	-207,000	-138,800
1683 . . . . .	-218,100	-138,800
1700 . . . . .	-218,000	-138,000
1800 . . . . .	-218,000	-135,400
1900 . . . . .	-217,800	-128,700
1953 . . . . .	-217,700	-126,200
1953 . . . . .	-215,600	-126,200
2000 . . . . .	-215,200	-123,900

## Phase changes of Oxide

T.P. ( $\alpha$ -trid. to  $\beta$ -trid.), 390°K;  $\Delta H = 40$  cal./moleT.P. ( $\beta$ -trid. to  $\beta$ -cris.), 1743°K;  $\Delta H = 30$  cal./moleM.P., 1953°K;  $\Delta H = 2150$  cal./mole

## Free Energy Equations:

Reaction	Range of Validity, °K
1) Si (c) + O <sub>2</sub> (g) = SiO <sub>2</sub> ( $\alpha$ -quartz)	298.16-848
$\Delta F_T^\circ = -210,070 + 3.98T \log T - 3.32 (10^{-5}T^2) + 6.05 (10^{-5}T^{-1}) + 34.59T$	
2) Si (c) + O <sub>2</sub> (g) = SiO <sub>2</sub> ( $\beta$ -quartz)	848-1683
$\Delta F_T^\circ = -209,920 - 3.36T \log T - .19 (10^{-5}T^2) - .745 (10^{-5}T^{-1}) + 53.44T$	
3) Si (l) + O <sub>2</sub> (g) = SiO <sub>2</sub> ( $\beta$ -quartz)	1683-1803
$\Delta F_T^\circ = -219,000 + .58T \log T - .47 (10^{-5}T^2) - .20 (10^{-5}T^{-1}) + 46.58T$	
4) Si (l) + O <sub>2</sub> (g) = SiO <sub>2</sub> (l)	1883-2000
$\Delta F_T^\circ = -228,590 - 15.66T \log T + 103.97T$	
5) Si (c) + O <sub>2</sub> (g) = SiO <sub>2</sub> ( $\alpha$ -cristobalite)	298.16-523
$\Delta F_T^\circ = -207,330 + 19.96T \log T - 9.75 (10^{-5}T^2) - .745 (10^{-5}T^{-1}) - 9.78T$	

# Silicon Dioxide, SiO<sub>2</sub> (page 4)

- 6) Si (c) + O<sub>2</sub> (g) = SiO<sub>2</sub> (β-cristobalite) 523-1683  
 $\Delta F_T^\circ = -209,820 - 3.34T \log T - .24 (10^{-3}T^2) - .745 (10^6T^{-1}) + 53.35T$
- 7) Si (l) + O<sub>2</sub> (g) = SiO<sub>2</sub> (β-cristobalite) 1583-2000  
 $\Delta F_T^\circ = -218,900 + .60T \log T - .52 (10^{-3}T^2) - .20 (10^6T^{-1}) + 46.49T$
- 8) Si (c) + O<sub>2</sub> (g) = SiO<sub>2</sub> (α-tridymite) 298.16-390  
 $\Delta F_T^\circ = -207,030 + 22.29T \log T - 11.67 (10^{-3}T^2) - .745 (10^6T^{-1}) - 15.64T$
- 9) Si (c) + O<sub>2</sub> (g) = SiO<sub>2</sub> (β-tridymite) 390-1683  
 $\Delta F_T^\circ = -209,350 - 1.59T \log T - .52 (10^{-3}T^2) - .745 (10^6T^{-1}) + 47.86T$
- 10) Si (l) + O<sub>2</sub> (g) = SiO<sub>2</sub> (β-tridymite) 1683-1953  
 $\Delta F_T^\circ = -218,430 + 2.35T \log T - .82 (10^{-3}T^2) - .20 (10^6T^{-1}) + 41.00T$

Entropy, cal./deg./mole at 298°K: quartz, 10.00 1, 9  
cristobalite, 10.19 1  
tridymite, 10.36 1

See Table d

Melting Point:

See Crystalline Form

Heat of Fusion, Kcal./mole at 298°K: quartz, 2.04 9  
cristobalite, 3.6 ± 0.5 24

Boiling Point: 2503°K (2230°C) 1

Heat of Vaporization: —

Heat of Sublimation: —

## d. HEAT CONTENT AND ENTROPY OF SiO<sub>2</sub> (cristobalite) (Base, α-crystals at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	1210	3.48	1200 . . . . .	14,080	20.90
500 . . . . .	2560	6.48	1300 . . . . .	15,790	22.27
523 (α) . . . .	2910	7.16	1400 . . . . .	17,510	23.54
523 (β) . . . .	3110	7.54	1500 . . . . .	19,240	24.74
600 . . . . .	4310	9.62	1600 . . . . .	20,990	25.87
700 . . . . .	5850	12.05	1700 . . . . .	22,750	26.93
800 . . . . .	7460	14.20	1800 . . . . .	24,520	27.95
900 . . . . .	9090	16.12	1900 . . . . .	26,320	28.92
1000 . . . . .	10,730	17.85	2000 . . . . .	28,120	29.84
1100 . . . . .	12,390	19.42			

### SiO<sub>2</sub> (α-cristobalite)

Enthalpy: H<sub>T</sub> - H<sub>298.15</sub> = 4.28T + 10.53 × 10<sup>-5</sup>T<sup>2</sup> - 2212 (10 percent; 298-523°K)

Heat Capacity: C<sub>p</sub> = 4.28 + 21.06 × 10<sup>-5</sup>T; ΔH<sub>523</sub> (transition) = 200

Silicon Dioxide, SiO<sub>2</sub> (page 5)

SiO<sub>2</sub> (β-cristobalite) :

Enthalpy:  $H_T - H_{298.15} = 14.40T + 1.02 \times 10^{-3}T^2 - 4696$  (0.2 percent ; 523-2000°K)

Heat Capacity:  $C_p = 14.40 + 2.04 \times 10^{-3}T$

e. HEAT CONTENT AND ENTROPY OF SiO<sub>2</sub>(gl)  
(Base, glass at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	1230	3.54	1300	15,450	21.57
500	2550	6.48	1400	17,240	22.90
600	3950	9.03	1500	19,080	24.17
700	5430	11.31	1600	20,980	25.39
800	6990	13.39	1700	22,930	26.57
900	8610	15.30	1800	24,920	27.71
1000	10,280	17.06	1900	26,950	28.81
1100	11,980	18.68	2000	29,010	29.87
1200	13,700	20.17			

SiO<sub>2</sub> (gl) :

Enthalpy:  $H_T - H_{298.15} = 13.38T + 1.84 \times 10^{-3}T^2 + 3.45 \times 10^3T^{-1} - 5310$   
(0.4 percent ; 298-2000°K)

Heat Capacity:  $C_p = 13.38 + 3.68 \times 10^{-3}T^2 - 3.45 \times 10^3T^{-2}$

f. HEAT CONTENT AND ENTROPY OF SiO<sub>2</sub>(tridymite)  
(Base, α-crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350	585	1.81	1100	12,250	19.25
390 (α)	1085	3.16	1200	13,940	20.72
390 (β)	1125	3.26	1300	15,650	22.09
400	1270	3.63	1400	17,370	23.37
500	2710	6.84	1500	19,100	24.56
600	4170	9.50	1600	20,850	25.69
700	5710	11.87	1700	22,610	26.75
800	7320	14.02	1800	24,390	27.77
900	8950	15.94	1900	26,180	28.74
1000	10,590	17.67	2000	27,980	29.66

SiO<sub>2</sub> (α-tridymite)

Enthalpy:  $H_T - H_{298.15} = 3.27T + 12.40 \times 10^{-3}T^2 - 2077$  (0.2 percent ; 298-390°K)

Heat Capacity:  $C_p = 3.27 + 24.80 \times 10^{-3}T$ ;  $\Delta H_{390}$  (transition) = 40

SiO<sub>2</sub> (β-tridymite) :

Enthalpy:  $H_T - H_{298.15} = 13.64T + 1.32 \times 10^{-3}T^2 - 4395$  (0.7 percent ; 590-2000°K)

Heat Capacity:  $C_p = 13.64 + 2.64 \times 10^{-3}T$

# Silicon Dioxide, SiO<sub>2</sub> (page 6)

Transition Point, °K: c, III 91 → c, II 846 → c, I 1140 tridymite, c, I

Heat of Transition, Kcal./mole: 0.15 0.12

Heat Capacity, cal./deg./mole: (solid) 19.62  
(gas) 7.14

See Tables d, e, f

Decomposition Temperature: At 1173–1428°K and at 1900°K the gas is SiO.

Decomposition Products: —

Dissociation Pressures: —

Vapor Pressure: —

Press. mm.	10	40	100	400	760	M.P.
Temp. °C	1732	1867	1969	2141	2227	1710

X-Ray Crystallographic Data:

Substance	System	Space Group	a	b	c	Molecules/ Unit Cell
β-cristobalite (at 290°C)	cub	O <sub>h</sub>	7.12			8
α-quartz	hex	D <sub>3h</sub> <sup>+</sup> or D <sub>3d</sub> <sup>+</sup>	4.903		5.393	3
β-quartz (at 600°C)	hex	D <sub>3h</sub> <sup>+</sup> or D <sub>3d</sub> <sup>+</sup>	5.01		5.47	3
α-tridymite	rhomb	D <sub>2h</sub> <sup>+</sup>	9.88	17.1	16.3	64
β-tridymite	hex	D <sub>3h</sub> <sup>+</sup>	5.03		8.22	64

Hygroscopicity: —

Solubility Data: Soluble in HF; very slightly soluble in alkalies. Insoluble in water and acids. For the effect of particle size on the soly. of amorphous SiO<sub>2</sub> in water see Addnl. Ref. 1.

Health Hazard: Prolonged exposure to SiO<sub>2</sub> dust causes disabling pulmonary fibrosis (silicosis). The presence of other dusts may reduce the action of the silica; this is particularly so with small amounts of Al dust.

M.A.C., million particles per cu. ft. of air for an 8 hr. working day.

Silica—high (above 50% free SiO<sub>2</sub>): 5  
medium (5 to 50% free SiO<sub>2</sub>): 20  
low (below 5% free SiO<sub>2</sub>): 50

Safety Classifications: none listed in OSM, ICC or U.N.

Fire and Explosion Hazard: —

Electrostatic Sensitivity: —

## TEMPERATURE STABILITY OF ALLOTROPIC FORMS OF SiO<sub>2</sub>

Form

Low (α) quartz  
High (β) quartz

Low (α) tridymite

Temperature Stability

Stable at atmospheric temp. and up to 575°C.  
Stable from 573 to 870°C; capable of existence above 870°C but is not stable.  
Capable of existence at atmospheric temp. and up to 117°C, but is not stable in this range.

**Silicon Dioxide, SiO<sub>2</sub> (page 7)**

Lower-high ( $\beta_1$ ) tridymite	Capable of existence between 117 and 163°C but is not stable in this range.
Upper-high ( $\beta_2$ ) tridymite	Capable of existence above 163°C, and is stable from 870 to 1470°C; above 1470°C is again unstable; melts at 1670°C.
Low ( $\alpha$ ) cristobalite	Capable of existence above 163°C, and up to 200 to 275°C but is not stable in this range.
High ( $\beta$ ) cristobalite	Capable of existence above 200 to 275°C, and is stable from 1470 to 1710°C (M.P.).
Vitreous silica	Capable of existence at atmospheric temps. and up to 1000°C and above, where it begins to crystallize with measurable rapidity, but is an unstable undercooled liquid at all temps. below 1719°C.

Use in Pyrotechnics: A product resulting from burning silicon or silicon compounds.

**Additional References:**

- 1) G. B. Alexander, J. Phys. Chem. 61, 1563-64 (1957)
- 2) Ref. 44V15B
- 3) L. Brewer and D. F. Mastick, J. Chem. Phys. 19, 834 (1951)
- 4) "Crystal Chemistry in Ceramics: VI Polymorphism," W. Hauth Jr., Bull. Am. Ceram. Soc. 30, (5) 165-67 (1951). Cited by Ref. 65.
- 5) 97V1

**SODIUM, Na**  
(Natrium)

*Refs.*

Specification No.:	JAN-S-328	
Molecular Weight:	22.991	
Crystalline Form:	cubic	1
Color: Silvery metal when freshly cut; tarnishes rapidly on exposure to air, becoming dull and grey.		1, 29
Density, g./ml.:	(solid) 0.97 <sup>25°</sup>	1
Coefficient of Thermal Expansion, linear, -188° to +17°C:	6.2 × 10 <sup>-6</sup>	1
Heat of Formation, Kcal./mole at 298°K:	(monatomic gas) 25.9 (diatomic gas) 33.8	5
Free Energy of Formation, Kcal./mole at 298°K:	(monatomic gas) 18.595 (diatomic gas) 24.685	5
Entropy, cal./deg./mole, at 298°K:	(monatomic gas) 36.71 (diatomic gas) 33.8 (c) 12.21	5
See Tables a, b, and c		
Melting Point:	370.97°K (97.81°C)	5
Heat of Fusion, cal./mole:	622	4
Boiling Point:	1178°K (905°C)	4
Heat of Vaporization, cal./mole:	23,380	4
Transition Point:	—	
Heat of Sublimation, cal./mole:	(monatomic gas) 25,900 (diatomic gas) 33,800	5
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 1532	5
See Tables a, b, c, and d		
a. HEAT CONTENT AND ENTROPY OF Na (c, l, g)		4
(Base, crystals at 298.15°K)		

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
350 . . . . .	360	1.11	1178 (l) . . .	6340	11.47
371 (c) . . .	514	1.54	1178 (g) . . .	30,220	31.32
371 (l) . . .	1136	3.21	1200 . . . . .	30,380	31.41
400 . . . . .	1355	3.78	1300 . . . . .	30,825	31.80
500 . . . . .	2095	5.44	1400 . . . . .	31,325	32.18
600 . . . . .	2820	6.76	1500 . . . . .	31,320	32.52
700 . . . . .	3520	7.84	1600 . . . . .	32,315	32.84
800 . . . . .	4220	8.77	1700 . . . . .	32,815	33.14
900 . . . . .	4910	9.58	1800 . . . . .	33,310	33.42
1000 . . . . .	5595	10.31	1900 . . . . .	33,805	33.69
1100 . . . . .	6295	10.98	2000 . . . . .	34,305	33.94

## Sodium, Na (page 2)

Na (c) :

Enthalpy:  $H_T - H_{298.15} = 4.02T + 4.52 \times 10^{-3}T^2 - 1599$  (0.3 percent; 298–371°K)Heat Capacity:  $C_p = 4.02 + 9.04 \times 10^{-3}T$ 

Na (l) :

Enthalpy:  $H_T - H_{298.15} = 6.83T - 1.08 \times 10^5 T^{-1} - 1107$  (0.2 percent; 371–1178°K)Heat Capacity:  $C_p = 6.83 + 1.08 \times 10^5 T^{-2}$ 

Na (g) :

Enthalpy:  $H_T - H_{298.15} = 4.97T + 24,365$  (0.1 percent; 1178–2000°K)b. HEAT CONTENT AND ENTROPY OF Na (g)  
(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	505	1.46	1900	7960	9.20
500	1005	2.57	2000	8460	9.46
600	1500	3.48	2200	9455	9.93
700	1995	4.24	2400	10,450	10.37
800	2495	4.90	2600	11,450	10.77
900	2990	5.49	2800	12,455	11.14
1000	3490	6.01	3000	13,470	11.49
1100	3985	6.49	3500	16,055	12.29
1200	4480	6.92	4000	18,770	13.01
1300	4980	7.32	4500	21,700	13.70
1400	5475	7.69	5000	25,015	14.40
1500	5970	8.03	6000	33,755	15.98
1600	6470	8.35	7000	46,850	18.02
1700	6965	8.65	8000	65,295	20.45
1800	7460	8.93			

Na (g) :

Enthalpy:  $H_T - H_{298.15} = 4.97T - 1482$  (0.1 percent, 298–3000°K)c. HEAT CONTENT AND ENTROPY OF Na<sub>2</sub>(g)  
(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	920	2.64	1800	9240	13.51
500	1825	4.67	1400	10,185	14.21
600	2735	6.33	1500	11,185	14.87
700	3655	7.75	1600	12,090	15.48
800	4580	8.99	1800	14,010	16.61
900	5500	10.07	2000	15,945	17.63
1000	6435	11.06	2200	17,895	18.56
1100	7360	11.94	2400	19,860	19.41
1200	8305	12.76	2600	21,845	20.21

Sodium, Na (page 3)

$\text{Na}_2(\text{g})$

Enthalpy:  $H_T - H_{298.15} = 8.96T + 0.18 \times 10^{-5}T^2 + 0.10 \times 10^5T^{-1} - 2721$   
 (0.1 percent; 298-2600°K)

Heat Capacity:  $C_p = 8.96 + 0.36 \times 10^{-5}T - 0.10 \times 10^5T^{-2}$

Heat Capacity, cal./mole at 298°K: (solid) 6.74 (liquid) 7.50  
 (gas) (monatomic) 4.97  
 (diatomic) 8.96

d. HEAT CAPACITY OF SODIUM

Solid, 298-371°K

Liquid, 371-1163°K

Gas (monatomic), 1163-3000°K

T, °K	$C_p$ (cal./deg./mole)
298	6.74
300	6.75
400	7.52
600	7.10
800	6.90
1000	6.93
1100	7.01
1200-2000	4.97
2400	4.99
2800	5.04
3000	5.08

See equations above

Decomposition Temperature: —

Decomposition Products: —

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P. °C
Temp. °C	439	549	633	701	823	892	97.5

$$\log P = \frac{5220}{T} + 4.521, \text{ where } P = \text{atm. and } T = ^\circ\text{K}$$

X-Ray Crystallographic Data:

System	Space Group	a	Atoms/Unit Cell
cubic	$O_h$	4.282	2

Hygroscopicity: Reacts vigorously with water to form NaOH + H<sub>2</sub>

Caution: keep under kerosene.

Solubility Data: In water, alcohol:

decomposes

In benzene, ether:

insoluble

Health Hazard: Extremely caustic to all tissues. Reacts exothermally with the moisture of the body or tissue surfaces causing thermal and chemical burns.

Safety Classifications:

OSM:

class 2

ICC: Listed under "Explosives and Other Dangerous Articles" as a flammable solid; yellow label.



Sodium, Na (page 4)

Fire and Explosion Hazard: Metallic sodium has an autoignition temperature of 115° in dry air. It is dangerous when exposed to heat, flame, moisture, air, or oxidizing material. It reacts exothermally with the halogens, acids, and halogenated hydrocarbons.

Sodium must be kept dry to avoid explosions which may result from evolved hydrogen. When heated it emits toxic fumes of  $\text{Na}_2\text{O}$ . Metallic sodium should be stored in airtight, steel drums. To fight fire use soda ash, dry sodium chloride, powdered talc or graphite. Do not use  $\text{CCl}_4$  on fire as an explosion may result.

Electrostatic Sensitivity:

Use in Pyrotechnics: As a fuel and to color burning compositions yellow.

Additional References:

- 1) "Sodium, Its Manufacture, Properties and Uses," M. Sittig, Reinhold Publishing Corp., New York (1956). See especially the chapter on physical and thermodynamic properties.
- 2) "Determination of the Vapor Pressure of Sodium," M. MaKansi et al., *J. Phys. Chem.* 59, 40 (1955)
- 3) *C.A.* 37, 2578 (1943)

12, 14, 75,  
Addnl. Ref. 3

**SODIUM BICARBONATE,  $\text{NaHCO}_3$**   
(Sodium Acid Carbonate, Baking Soda, Sodium Hydrogen Carbonate)

Specification No.:	O-S-576B (technical grade)	Refs. 1, 11, 29
Molecular Weight:	84.02	
Crystalline Form:	monoclinic prisms	1
Color:	white	1
Density, g./ml.:	(solid) 2.159-2.22	1
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	(c) -226.5	1
Free Energy of Formation, Kcal./mole at 298°K:	(c) -203.6	1
Entropy, cal./deg./mole at 298°K:	24.4 ± .4	1, 3
See table below		
Melting Point:	loses $\text{CO}_2$ at 543°K (270°C)	1
Heat of Fusion:	—	
Boiling Point:	—	
Heat of Vaporization:	—	
Transition Point:	—	
Heat of Transition:	—	
Heat of Sublimation:	—	

**HEAT CONTENT AND ENTROPY OF  $\text{NaHCO}_3$**   
(Base, crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350 . . . . .	1140	3.52	400 . . . . .	2320	6.67

**$\text{NaHCO}_3(c)$  :**

Enthalpy:  $H_T - H_{298.15} = 10.19T + 18.03 \times 10^{-5}T^2 - 4641$  (0.3 percent; 298-400°K)

Heat Capacity:  $C_p = 10.19 + 36.06 \times 10^{-5}T$

Decomposition Temperature: Begins to lose  $\text{CO}_2$  at about 50°C, and at 100°C is converted to  $\text{Na}_2\text{CO}_3$ . In aqueous solution begins to break up into  $\text{CO}_2$  and  $\text{Na}_2\text{CO}_3$  at 20°C and completely on boiling.

Heat of Dissociation, cal./mole: 15,360 Addnl. Ref. 2

Vapor Pressure of dissociation to ( $\text{CO}_2 + \text{H}_2\text{O}$ ) is given by

$$\log \text{Pmm.} = 11.165 - \frac{3840}{T_{\text{abs.}}}$$

Addnl. Ref. 2

See also 42V7

**X-Ray Crystallographic Data:**

System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell
monoclinic	$C_{2h}$	6.19	6.72	6.49	$\beta = 120^\circ 42'$	4

**Sodium Bicarbonate, NaHCO<sub>3</sub> (page 2)**

Hygroscopicity: NaHCO <sub>3</sub> is stable in dry air. In the presence of moisture it gradually loses CO <sub>2</sub> and changes to NaHCO <sub>3</sub> ·Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O	62
Solubility Data: In water: 6.9 g./100 ml. at 0° and 16.4 g./100 ml. at 60°C	1
In alcohol: slightly soluble	
Health Hazard: nontoxic, large doses may cause alkalosis	93, 29
Safety Classifications:	
OSM: inert material	
ICC: not listed	
Fire and Explosion Hazard: not listed	
Electrostatic Sensitivity: none	
Use in Pyrotechnics: as a retardant	
Additional References:	
1) Ref. 52V10	
2) R. M. Caven and H. J. Sand, J. Chem. Soc. 99, 1359 (1911)	

**SODIUM NITRATE,  $\text{NaNO}_3$**   
(Soda Niter, Chile Niter, Chile Saltpeter, Nitratine, Cubic Niter)

Percent Oxygen:	56.46	
Specification No.:	MII -S-00322A	
The specification covers two classes: class 1, technical; and class 2, double refined. The two classes differ in purity.		
Molecular Weight:	85.01	
Crystalline Form:	trigonal or rhombohedral	1
Color:	colorless	1
Density, g./ml.: (solid) $d = 2.116 - 0.67 \times 10^{-5}t^\circ\text{C}$ (320–550°C)		40V2
Coefficient of Thermal Expansion (average from R.T. to M.P.):	$3.65 \times 10^{-4}$	31
Heat of Formation, Kcal./mole at 298°K:	(c) -111.54	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(c) -87.45	1, 9
Entropy, cal./deg./mole, at 298°K:	(c) 27.8	1, 9
See table below		
Melting Point:	579.2°K (306.1°C)	4
Heat of Fusion, cal./mole:	3490	4
Boiling Point:	decomposes	1
Transition Point:	$\alpha$ to $\beta$ 549.2°K (276.1°C)	4
Heat of Transition, cal./mole:	810	4
Heat of Sublimation:	—	

**HEAT CONTENT AND ENTROPY OF  $\text{NaNO}_3$  (c, 1)**  
(Base,  $\alpha$ -crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	2495	7.16	579.2 ( $\beta$ ) . .	9140	20.59
500 . . . . .	5575	14.01	579.2 (l) . .	12,630	26.62
549.2 ( $\alpha$ ) . .	7260	17.22	600 . . . . .	13,400	27.93
549.2 ( $\beta$ ) . .	8070	18.70	700 . . . . .	17,100	33.63

**$\text{NaNO}_3(\alpha)$ :**

Enthalpy:  $H_T - H_{298.15} = 6.34T + 26.66 \times 10^{-5}T^2 - 4260$  (1.0 percent; 298–549.2°K)

Heat Capacity:  $C_p = 6.34 + 53.32 \times 10^{-5}T$

**$\text{NaNO}_3(\beta)$ :**

Enthalpy:  $H_T - H_{298.15} = 35.70T - 11,536$  (0.1 percent; 549.2–579.2°K)

**$\text{NaNO}_3(l)$ :**

Enthalpy:  $H_T - H_{298.15} = 37.00T - 8800$  (0.1 percent; 579.2–700°K)

Heat Capacity, cal./deg./mole: (solid) 35.70  
(liquid) 37.00

See also table above

**Sodium Nitrate,  $\text{NaNO}_3$  (page 2)**

Decomposition Temperature: 380°C 1  
 For DTA and TGA see Refs. 33, 47  
 Decomposition Products:  $\text{Na}_2\text{O} + \text{NO}_2$  33, 47  
 Vapor Pressure: —  
 X-Ray Crystallographic Data:

System	Space Group	a	Axial Angle	Molecules/ Unit Cell	
rhombohedral	$D_{3h}^2$	6.3108	$\alpha = 47^\circ 15' 59''$	2	1, 97V6
at 280°C		6.56	$\alpha = 45^\circ 35'$		18
hexagonal		5.07	$\beta = 16.829$	6	97V6

Hygroscopicity: Deliquesces in moist air. Keep container well closed. 29

Critical R.H.: 82.7% at 20°C (purified material.) 32

Gain of purified material (41  $\mu$ ), at 70°F after 120 hours exposure:  
 (at 70% R.H.) 11% 33  
 (90% R.H.) 25.75%

Water absorbed by 2.000 g. at 25° (40–80 mesh): Addnl. Ref. 1

Hrs.	3	5½	7½	16
g. $\text{H}_2\text{O}$ absorbed	0.0713	0.1355	0.1970	0.3924

**Solubility Data:**

In water (g./100 ml.): 73 at 0°C; 180 at 100°C 12

In  $\text{NH}_3$ : very soluble

In glycerine and acetone: slightly soluble

Health Hazard: Moderately toxic. Large amounts taken internally may be fatal. 93, 12

**Safety Classifications:**

OSM: Class 1, packed and stored in original shipping containers.

Class 2, when not packed or stored in original shipping containers or equivalent.

ICC: Oxidizing material: yellow label.

Fire and Explosion Hazard: Sodium nitrate is a dangerous fire and explosion hazard. It can ignite on friction. When heated above 1000°C or when heated with reducing materials, particularly cyanides, it emits toxic fumes on decomposition. 12

Electrostatic Sensitivity: —

Use in Pyrotechnics: As an oxidizer, to impart a yellow color to burning compositions, and incendiary mixtures.

**Additional References:**

- 1) "Hygroscopic Properties of Sodium, Potassium and Ammonium Nitrates, Potassium Chlorate and Mercury Fulminate," G. B. Taylor and W. C. Cope, *Met. & Chem. Eng.* 15, 141 (1916)

# SODIUM OXALATE

Refs.

Formula:  $\text{Na}_2\text{C}_2\text{O}_4$   
 Specification No.: JAN-S-210  
 Specification: The spec. covers one technical grade and three classes based on differences in granulation using U.S. standard sieves.

Class	a	b	c
Through 420 micron (No. 40 sieve) %, min.	99		
Through 250 micron (No. 60 sieve) %, min.		99.9	
Through 148 micron (No. 100 sieve) %, min.			99.9

Molecular Weight:	134.01						
Crystalline Form:	crystalline powder	29					
Color:	white	29					
Density, g./ml.:	(solid) 2.34	1					
Coefficient of Thermal Expansion:	—						
Heat of Formation, Kcal./mole at 298°K:	-314.3	1, 9					
Free Energy of Formation:	—						
Entropy:	—						
Melting Point:	505°K (232.5°C)	1					
Heat of Fusion:	—						
Boiling Point:	—						
Transition Point:	—						
Heat of Sublimation:	—						
Heat Content or Enthalpy:	—						
Heat Capacity, cal./deg./mole:	(solid) 34	9					
Decomposition Temperature, °C:	480	Addnl. Ref. 1					
For DTA see Addnl. Refs. 2, 3							
Decomposition Products:	Na <sub>2</sub> CO <sub>3</sub> + CO						
Vapor Pressure:	—						
X-Ray Crystallographic Data:							
System	Space Group	a	b	c	β	Molecules/ Unit Cell	18
monoclinic	C <sub>2h</sub>	10.35	6.26	3.46	92° 54'	2	
Hygroscopicity: Spec. grade (20 μ)							33
Gain in wt. at 70% R.H. and 70°F in 120 hr. %:	0.02						
Gain in wt. at 90% R.H. and 70°F in 120 hr. %:	0.02						44V21
Material dried at 240°C is not hygroscopic							
Solubility Data: In water at 20°C.					3.7 g./100 g.		1
	100°C:				6.33 g./100 g.		
in alcohol:					insoluble		2°

**Sodium Oxalate (page 2)**

Health Hazard: A strong poison. Corrosive and produces local irritation. Taken orally has a caustic effect on the mouth, esophagus and stomach. Can cause severe damage to the kidneys. 12, 29

**Safety Classifications:**

OSM: not listed  
ICC: not listed

Fire and Explosion Hazard: Dangerous when heated to decomposition: emits toxic fumes. 12

**Electrostatic Sensitivity:** —

Use in Pyrotechnics: As a retardant and to impart a yellow color to burning compositions. 17

**Additional References:**

- 1) C.A. 48, 1891 (1954)
- 2) C.A. 49, 14461 (1955)
- 3) C.A. 50, 7672 (1956)

**SODIUM OXIDE, Na<sub>2</sub>O**  
(Sodium Monoxide)

Specification No.:	—	Refs.
Molecular Weight:	61.99	1
Crystalline Form:	deliquesces in air	1
Color:	white	1
Turns yellow on heating		50V12
Density, g./ml.:	(solid) 2.27	1
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	(c) -99.4 ± 1.5	2, 9
See Table a		
Free Energy of Formation, Kcal./mole at 298°K:	(c) -89.9 ± 1.9	2
See Table a		

**a. HEAT AND FREE ENERGY OF FORMATION OF Na<sub>2</sub>O (c, l)**

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.15 . . . . .	-99,400 (± 1500)	-89,900 (± 1900)
371 . . . . .	-99,400	-87,500
371 . . . . .	-100,700	-87,500
400 . . . . .	-100,700	-86,500
500 . . . . .	-100,600	-83,000
600 . . . . .	-100,600	-79,400
700 . . . . .	-100,500	-75,900
800 . . . . .	-100,400	-72,400
900 . . . . .	-100,200	-69,000
1000 . . . . .	-99,900	-65,500
1100 . . . . .	-99,500	-62,100
1187 . . . . .	-99,100	-59,100
1187 . . . . .	-145,300	-59,100
1190 . . . . .	-145,300	-58,900
1190 . . . . .	-132,200	-58,900
1200 . . . . .	-138,100	-58,200
1300 . . . . .	-137,100	-51,600
1400 . . . . .	-136,100	-45,100
1500 . . . . .	-135,100	-38,600
1600 . . . . .	-134,100	-32,200
1700 . . . . .	-133,100	-25,900
1800 . . . . .	-132,100	-19,600
1900 . . . . .	-131,100	-13,400
2000 . . . . .	-130,100	-7,200

Phase Changes of Metal

M.P., 371°K; Δ H = 626 cal./g.-atom

B.P., 1187°K; Δ H = 25,120 cal./g.-atom



Sodium Oxide, Na<sub>2</sub>O (page 2)

Entropy, cal./deg./mole at 298°K: See Table b	(c) 17.4	9
Melting Point:	1190°K (917°C)	2
Heat of Fusion, cal./mole:	7140	2
Boiling Point:	sublimes at 1548°K (1275°C)	1
Heat of Vaporization, Kcal./mole:	149	
Transition Point:	—	
Heat of Sublimation:	—	

b. HEAT CONTENT AND ENTROPY OF Na<sub>2</sub>O (c)  
(Base, crystals at 298.15°K)

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	1750	5.05	800 . . . . .	9350	18.16
500 . . . . .	3660	9.17	900 . . . . .	11,350	20.52
600 . . . . .	5500	12.63	1000 . . . . .	13,500	22.78
700 . . . . .	7400	15.56	1100 . . . . .	15,750	24.98

Na<sub>2</sub>O (c) :Enthalpy:  $H_T - H_{298.15} = 15.70T + 2.70 \times 10^{-5}T^2 - 4921$  (0.7 percent; 298–1100°K)Heat Capacity:  $C_p = 15.70 + 5.40 \times 10^{-5}T$ Na<sub>2</sub>O<sub>2</sub>(c) :Heat Capacity:  $C_p = 21.35$  (298°K)

## Free Energy Equations:

Reaction	Range of Validity, °K
1) $2 \text{ Na (c)} + \frac{1}{2} \text{ O}_2 \text{ (g)} = \text{Na}_2\text{O (c)}$ $\Delta F_T^\circ = -95,820 - 7.51T \log T + 5.47 (10^{-5}T^2) - .10 (10^6T^{-1}) + 50.43T$	298.16–371
2) $2 \text{ Na (l)} + \frac{1}{2} \text{ O}_2 \text{ (g)} = \text{Na}_2\text{O (c)}$ $\Delta F_T^\circ = -100,150 + 4.97T \log T - 2.45 (10^{-5}T^2) - .10 (10^6T^{-1}) + 22.19T$	371–1187
3) $2 \text{ Na (γ)} + \frac{1}{2} \text{ O}_2 \text{ (g)} = \text{Na}_2\text{O (c)}$ $\Delta F_T^\circ = -156,200 - 20.72T \log T + 145.48T$	1187–1190
4) $2 \text{ Na (g)} + \frac{1}{2} \text{ O}_2 \text{ (g)} = \text{Na}_2\text{O (l)}$ $\Delta F_T^\circ = -150,250 - 23.03T \log T + 147.58T$	1190–2000

Heat Capacity, cal./deg./mole at 298°K: (solid) 17.24

See Table b

Decomposition Temperature:

above 400°C

Addnl. Refs.  
1, 2

Decomposition Products:

Na + O on vaporization

Addnl. Refs.  
1, 2

Vapor Pressure (of alkali oxide and alkali metal in equil. with solid alkali oxide) atm. at 1000°K:

(calcd.)  $10^{-15}$ 

Addnl. Ref. 3

**Sodium Oxide, Na<sub>2</sub>O (page 3)**

**X-Ray Crystallographic Data:**

<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>Molecules/Unit Cell</i>	
cubic		5.55		18

**Hygroscopicity:** Na<sub>2</sub>O reacts vigorously with water with considerable evolution of heat. Keep containers tightly closed.

**Solubility Data:** In water and alcohol: decomposes  
Reacts to neutralize acids.

**Health Hazard:** Very caustic and dangerous to all tissues. To minimize its effects, wash the area with large volumes of water. Injured person should see a physician.

**Caution:** Do not handle with bare hands. Avoid contact with skin.  
**M.A.C., mg./m.<sup>3</sup> of air:** 2

**Safety Classifications:**

<b>OSM:</b>	not specifically mentioned	
<b>ICC:</b>	not specifically mentioned	
Alkaline caustic liquids (not otherwise specified) are classed as corrosive liquids and listed under "Explosives and Other Dangerous Articles."		
<b>Coast Guard:</b>	hazardous material	
<b>UN:</b>	class 8 (alkaline corrosives)	

**Fire and Explosion Hazard:** Sodium hydroxide formed by the action of water on Na<sub>2</sub>O may become a fire hazard when mixed with nitro compounds and other materials. (This hazard must be even greater with powdered, solid Na<sub>2</sub>O.)

**Electrostatic Sensitivity:** —

**Use in Pyrotechnics:** Product of the burning of many sodium compounds

**Additional References:**

- 1) "Sodium, Its Manufacture, Properties and Uses," M. Sittig, Reinhold Publishing Co., New York (1956)
- 2) "The Vapor Pressures of Lithium and Sodium Oxides," L. Brewer and J. Margrave, *J. Phys. Chem.* 59, 421 (1956)
- 3) "Stability of Gaseous Alkali and Alkaline Earth Oxides," L. Brewer and D. F. Mastick, *J. Am. Chem. Soc.* 73, 2045 (1951)

**STEARIC ACID,  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$  or  $\text{C}_{17}\text{H}_{35}\text{COOH}$**   
(Octadecanoic Acid, N-Octadecyclic Acid)

Specification No.: MIL-A-271

The spec. covers two grades: Grade I in loading ammo. Grade II used as a lubricant in the pelleting of explosives.

Molecular Weight: 284.47

Crystalline Form: monoclinic leaflets

Color: colorless

At room temperature stearic acid is a white, fairly hard, wax-like material. It is usually obtained either from fats and oils by hydrolysis and distillation or from oleic acid by hydrogenation. Pearl stearic acid is the material in free flowing powdered bead form for compounding purposes. Stearic acid is also marketed in cakes, powder or flake form, as single, double, or triple-pressed. Successive chillings and pressings remove more of the unsaturated liquid oils (particularly oleic acid), thus raising the melting point and giving a whiter, purer product. Synthetic stearic acid is also made by hydrogenation of unsaturated animal and fish oils.

Density, g./ml.: (solid) 847 at 69°C

Coefficient of Thermal Expansion, cubical,  
33.8–44.5°C:  $81 \times 10^{-6}$

Heat of Formation, Kcal./mole at 13°C,  
at constant press.: -223.8  
at constant vol.: -212.8

Free Energy of Formation: —

Entropy: —

Melting Point: 342.5°K (69.4°C)  
342.7°K (69.6°C)

Heat of Fusion, cal./g.: 47.6

Boiling Point: 656°K (383°C)

Transition Point: —

Heat of Sublimation: —

Heat Content or Enthalpy: —

Heat Capacity: —

Decomposition Temperature and Products: For DTA see Addnl. Ref. 3

Vapor Pressure, mm. at 60°C:  $1.42 \times 10^{-6}$

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	173.7	225.0	263.3	291.0	343.0	370.0d	69.3

X-Ray Crystallographic Data:

System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell
monoclinic	$\text{C}_{2h}^4$ or $\text{C}_{2h}^5$	5.546	7.381	48.84	$\beta = 63^\circ 38'$	4
		5.68	7.39	50.07	$\beta = 60^\circ$	

Hygroscopicity: —

Refs.

1

1

1

16, 22

31

1

1

Addnl. Ref. 2

1

1

Addnl. Ref. 1

1

1

Addnl. Ref. 2

**Stearic Acid (page 2)**

<b>Solubility Data:</b> In water: 0.00029 g./100 g. at 20°C; 0.034 at 25°C and 0.1 g./ml. at 37°C		1, 29
In alcohol:	2.5 g./100 ml.	
In ether:	very soluble	
In CHCl <sub>3</sub> , CCl <sub>4</sub> , CS <sub>2</sub> , toluene:	soluble	
For additional solvent data see Addnl. Ref. 2		
<b>Health Hazard:</b> Negligible. Used to coat medicinal pills and in face creams.		29
<b>Safety Classifications:</b>		
OSM:	not listed	
ICC:	not listed	
<b>Fire and Explosion Hazard:</b> Combustible. To fight fire use water, foam, dry chemical, or carbon tetrachloride.		67, 75
<b>Electrostatic Sensitivity:</b>		—
Specific Heat, cal./g. at 15°C:	0.399	1
Liquid at 74–137°C:	0.550	
Refractive Index, at 80.2°C:	1.4299	1
Heat of Combustion, Kcal./mole (H <sub>2</sub> O liquid) at 20°C:	2711.8	1
Flash Point, °F:	(closed cup) 385 (open cup) 425	75
Ignition Temperature, °F:	743	67, 71
Neutralization Value:	197.23	Addnl. Ref. 2
Use in Pyrotechnics:	as a fuel, retardant, binder, and lubricant	
<b>Additional References:</b>		
1) "The Vapor Pressure of Some Solid Organic Compounds," R. L. Littlewood, J. Chem. Soc. 1957, 2419		
2) "Fatty Acids," K. S. Markley, Ed., Interscience Pub. Co., New York (1960)		
3) J. Phys. Chem. 60 1487 (1956)		
4) L. Médard, Mém. artillerie franç. 28, 465 (1954)		

# STRONTIUM CHLORIDE, SrCl<sub>2</sub>

Refs.

Specification No.:	—	
Molecular Weight:	158.54	
Crystalline Form:	cubic	1A
Color:	colorless	1A
Density, g./ml.:	(solid) 3.052	1A
(liquid) $D_t = 2.69 - 0.00045$ (to 900°C)		
Temp. °C	900	950
	1000	1050
Density	2.69	2.67
	2.645	2.62
Coefficient of Thermal Expansion, cubic at 870°C:	$166 \times 10^{-8}$	44S29
Heat of Formation, Kcal./mole at 298°K:	(c) -198.0	9, 24A
Free Energy of Formation, Kcal./mole at 298°K:	(c) -186.7	9
	-187.5	6
Entropy, cal./deg./mole at 298°K:	28	9, 31A
	31.7	6
Melting Point, °C:	873	1A, 24A
	875	41
Heat of Fusion, Kcal./mole at 1148°K (875°C):	4.2	44S29
	4.1	9, 41, 6
	$4.1 \pm 0.6$	24A
Boiling Point, °C:	1300	44S29
	1250	52
Heat of Vaporization, Kcal./mole:	55	6
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity, cal./deg./mole:	(solid) 18.9	9
$C_p = 18.20 + 2.45 \times 10^{-5}$ (est'd over 298 - 1145°K)		
See also Ref. 24A		
Decomposition Temperature: Noticeable above approx. 955°C		44S29
Heating in air or O <sub>2</sub> at red heat slowly changes the chloride to the oxide		52V11, 54V3
Decomposition Products:	—	
Vapor Pressure:	—	
X-Ray Crystallographic Data:		
System	Space Group	$a$
cubic	O <sub>h</sub>	6.9767
		Molecules/Unit Cell
		97V4
Hygroscopicity:		44S29
	hygroscopic	52V11
	very hygroscopic	

**Strontium Chloride, SrCl<sub>2</sub> (page 2)**

<b>Solubility Data:</b> In H <sub>2</sub> O, g./100 ml. 43.5 at 0°C and 100.8 at 100°C	1A
In absolute alcohol, acetic acid:	very slightly soluble
In NH <sub>3</sub> :	insoluble
<b>Health Hazard:</b> Probably slight. The Sr ion has a low order of toxicity.	12
<b>Safety Classifications:</b>	
OSM:	not listed
ICC:	not listed
<b>Fire and Explosion Hazard:</b>	—
<b>Electrostatic Sensitivity:</b>	—
<b>Use in Pyrotechnics:</b>	to color burning compositions crimson

# STRONTIUM NITRATE, $\text{Sr}(\text{NO}_3)_2$

Refs.

Specification No.:	MIL-S-20322	
The spec. covers one grade and three classes which differ in granulation.		
Molecular Weight:	211.65	
Crystalline Form:	cubic	1
Color:	colorless	1
Density, g./ml.:	(solid) 2.986	1
Coefficient of Thermal Expansion, linear, 30–75°C:	$\alpha = 3.22 \times 10^{-5}$	44S29 sup
Heat of Formation, Kcal./mole at 298°K:	–233.25	1, 9
Free Energy of Formation, Kcal./mole at 298.16°K:	–185.8	86
Entropy, cal./mole at 298.16°K:	47.4	86
Melting Point:	918°K (645°C) 891°K (618°C)	9 47
Heat of Fusion:	—	
Boiling Point:	decomposes 580–600°C	Addnl. Ref. 1
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity, cal./deg./mole:	(solid) 38.3 (290–320°K)	4
Decomposition Temperature, °C:	580–600	Addnl. Ref. 1
For DTA and TGA see Ref. 33		
Vigorous bubbling at 672°C		47
Decomposition Products:	SrO + NO <sub>2</sub> ; toxic fumes emitted	47
Vapor Pressure:	—	
X-Ray Crystallographic Data:		
System	Space Group	<i>a</i>
cubic	T <sub>h</sub> <sup>6</sup>	7.81
		Molecules/Unit Cell
		4
Hygroscopicity (gain, mg./g., at R.T. after equilibrium has been established in a vacuum desiccator):		32
% R.H.	65	75
	24 hr.    equil.	24 hr.    equil.
Purified	—    0.3	—    0.5
Spec. grade	0.3    <.1	0.1    0.2
		86
		24 hr.    equil.
		2. hr.    equil.
		—    —
		312.6    —
Critical R.H.:		
purified 82.7% at 20°C spec. grade 82.9% at 26.2°C		
Solubility Data: In water (g./100 ml.) 40.1 at 0° and 100 at 90°C		
In abs. alcohol, NH <sub>3</sub> :		
In acetone:		
very slightly soluble		
slightly soluble		

**Strontium Nitrate,  $\text{Sr}(\text{NO}_3)_2$  (page 2)**

**Health Hazard:** Moderately toxic. Large amounts taken by mouth may have fatal effects.  $\text{Sr}(\text{NO}_3)_2$  emits toxic fumes on decomposition. 93, 12

**Safety Classifications:**

OSM: Class 1, in original containers.

Class 2 when not packed or stored in original shipping containers or equivalent.

ICC: Oxidizing material; yellow label.

**Fire and Explosion Hazard:** A fire and explosion hazard. As an oxidizer it can give up its oxygen to other materials to produce a vigorous reaction which may result in detonation. Toxic fumes are emitted on decomposition. 12, 14

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:** An oxidizer and to impart a crimson color to burning compositions. (Nonhygroscopic strontium nitrate is used in tracer and pyrotechnic compositions that are sensitive to deterioration by moisture.) 17

**Additional References:**

- 1) C.A. 49, 12932 (1955)



**STRONTIUM OXALATE ANHYDROUS AND MONOHYDRATE,  
SrC<sub>2</sub>O<sub>4</sub> and SrC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O**

*Refs.*

Specification No.: MIL-S-12210

The spec. covers both the anhydrous salt and the monohydrate: Grade A, anhydrous, and Grade B, hydrated. The two grades differ also in granulation.

Molecular Weight: (anhydrous) 183.65  
(monohydrate) 193.67

Crystalline Form: ———

Color: colorless

1

Density, g./ml.: ———

Heat of Formation, Kcal./mole at 18°C, anhydrous:  
at constant press.: -327.7  
at constant vol.: -326.5

Addnl. Ref. 1

Free Energy of Formation, Kcal./mole at 18°C, monohydrate:  
(c) -360.8

1

Entropy: ———

Melting Point: See Decomposition Temperature below

Heat of Fusion: ———

Boiling Point: ———

Transition Point: ———

Heat of Sublimation: ———

Heat Content or Enthalpy: ———

Heat Capacity: ———

Decomposition Temperature: TGA. The hydrate begins to lose H<sub>2</sub>O at 43°C.  
All the water is off by 177°C. On further heating the weight remains constant up to around 400°C.

Addnl. Ref. 2

Decomposition Products: Dissociates into SrCO<sub>3</sub> and dangerous CO over the range 400-520°C.  
See graph below

Addnl. Ref. 2

Vapor Pressure: ———

X-Ray Crystallographic Data for SrC<sub>2</sub>O<sub>4</sub>·2½ H<sub>2</sub>O

System	Space Group	a	c	Molecules/Unit Cell
tetragonal	C <sub>4h</sub>	12.795	7.509	

18V2

Hygroscopicity: ———

Solubility Data: For SrC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O, required for solution of 1 part: 2000 parts of water, 1900 parts of 3.5% acetic acid, 1115 part of 23% acetic acid, less soluble in 35% acetic acid. Readily soluble in dilute HCl or HNO<sub>3</sub>.

29

1

Health Hazard: Highly toxic. Corrosive and produces local irritation. When taken orally may have a caustic effect on the mouth, esophagus and stomach.

12

93

Safety Classifications:

OSM:

not listed

ICC:

not listed

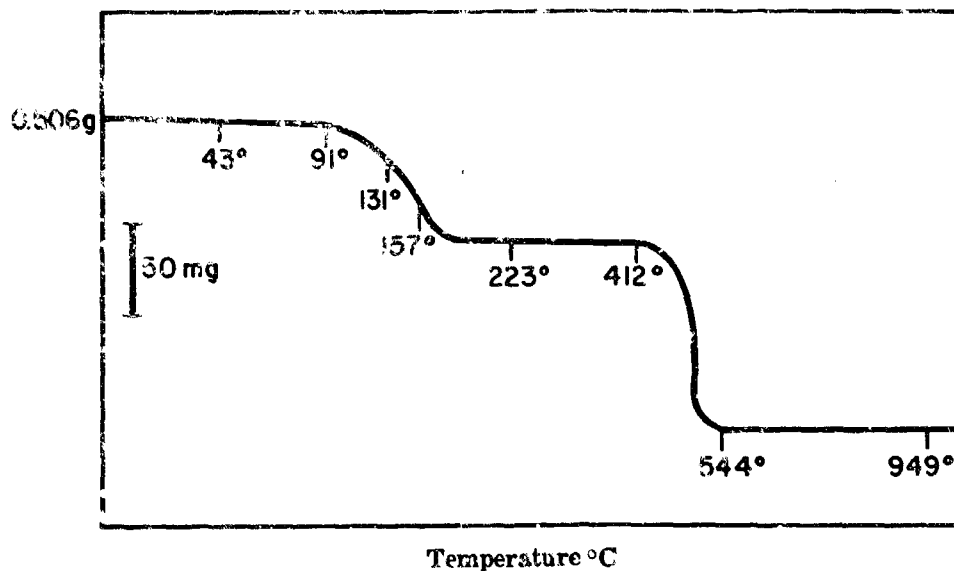
**Strontium Oxalate Anhydrous and Monohydrate (page 2)**

**Fire and Explosion Hazard:** Dangerous when heated to decomposition. Emits poisonous carbon monoxide. 12

**Electrostatic Sensitivity:** —

**Use in Pyrotechnics:**  $\text{SrC}_2\text{O}_4$  and  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  are used as retardants and to impart a scarlet color to burning compositions. 17

**PYROLYSIS OF  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$**



Addnl. Ref. 2

**Additional References:**

- 1) L. Médard, *Mém artillerie franç.* 28, 467 (1954)
- 2) S. Peltier and C. Duval, *Anal. Chem. Acta.* 1, 358 (1947)

# STRONTIUM PERCHLORATE, $\text{Sr}(\text{ClO}_4)_2$

Refs.

Specification No.:	—	
Molecular Weight:	286.54	
Percent Oxygen:	44.67	
Crystalline Form:	—	
Color:	colorless	1
Density, g./ml.:	—	
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	-184 (estd.)	72
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	—	
Heat of Fusion:	—	
Boiling Point:	—	
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature: Vigorous decomposition at 477°C. For DTA and TGA see Ref. 33		47
Decomposition Products:	—	
Vapor Pressure:	—	
X-Ray Crystallographic Data:	—	
Hygroscopicity:	—	
Solubility Data: In water, 310 g./100 ml. at 25°C; very soluble in hot water		1
Solubility in Organic Solvents at 25°C:		
Solvent	g./100 g. solvent	72, 77
Methyl alcohol	212.01	
Ethyl alcohol	180.66	
Acetone	150.06	
Ethyl acetate	136.93	
Ethyl ether	insoluble	
Health Hazard: Avoid contact. Irritating to skin and mucous membrane.		12
Safety Classifications:		
OSM: Class 1, Class 2 when not packed or stored in original shipping containers or equivalent.		
ICC: Oxidizing material; yellow label. Listed under "Explosives and Other Dangerous Articles."		
Fire and Explosion Hazard: Can be exploded by shock, heat, or chemical action. It is an explosive hazard when mixed with carbonaceous materials, finely divided metals, or sulfur. It emits highly toxic fumes. Fires involving the perchlorate alone may be fought with water.		12, 14
Use in Pyrotechnics: As an oxidizer and to impart a scarlet color to burning compositions.		

# STRONTIUM PEROXIDE, SrO<sub>2</sub>

Refs.

Percent Oxygen: 26.75  
Specification No.: JAN-S-612

Covers two grades that differ in purity and granulation.

Molecular Weight: 119.63  
Crystalline Form: powder  
Color: white  
Density, g./ml.: (solid) 4.56

1

Coefficient of Thermal Expansion: —

1

Heat of Formation, Kcal./mole at 298°K: -153.6  
See table below

1, 9

Free Energy of Formation, Kcal./mole at 298°K: -141  
See table below

2

## HEAT AND FREE ENERGY OF FORMATION OF SrO<sub>2</sub>(c)

4

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16 . . . .	-153,500 (± 5000)	-141,000 (± 6000)
400 . . . . .	-153,000	-137,000
500 . . . . .	-153,000	-133,000
600 . . . . .	-152,500	-129,000
700 . . . . .	-152,000	-125,000
800 . . . . .	-151,500	-121,500
900 . . . . .	-151,000	-117,500
1000 . . . . .	-150,500	-114,000

Free Energy Equation:

Reaction:  $\text{Sr (c)} + \text{O}_2 \text{ (g)} = \text{SrO}_2 \text{ (c)}$   
Range of Validity, °K: 298.16-1000  
 $\Delta F^\circ = -155,510 - 11.40T \log T + .305 (10^{-6}T^2) + .675 (10^{-6}T^{-1}) + 75.44T$

Entropy, cal./deg./mole at 298°K: 14.8  
For calculation see thermodynamic equation in Ref. 2

6

Melting Point: decomposes at 488°K  
(215°C)

6, 8

Heat of Fusion: —

Boiling Point: —

Transition Point: —

Heat of Sublimation: —

Heat Content or Enthalpy:  
For calculation see thermodynamic equation in Ref. 2

Heat Capacity:  
For calculation see thermodynamic equation in Ref. 2

**Srrentium Peroxide, SrO<sub>2</sub> (page 2)**

Decomposition Temperature:

dissociates at  
357°C  
480°C  
410°C and TGA

Addnl. Ref. 2  
Addnl. Ref. 3  
Addnl. Ref. 4

Decomposition Products:

Vapor Pressure: Dissociation Pressure between 322 and 600° is given by

$$P_{\text{atm}} = \frac{20280}{4.571T} - 0.010T + 1.75T + 2.8$$

Addnl. Ref. 1

Press. mm.	360	529	561	673
Temp. °C	328	342	344	351
Q (cal./g.)	19280	19310	19290	19290

Where Q<sub>o</sub> = heat of reaction for the equation  
2 SrO + O<sub>2</sub> = 2 SrO<sub>2</sub> + Qcal

Addnl. Ref. 2

Dissociation Pressure (to SrO + O<sub>2</sub>) is given as

$$\log p_{\text{mm}} = - \frac{19290}{4.571T} + 1.75 \log T - 0.0016T + 2.8$$

Addnl. Ref. 2

X-Ray Crystallographic Data:

System	Space Group	a	c	Molecules/Unit Cell
tetragonal	D <sub>2h</sub> <sup>16</sup>	5.02	6.55	4
		5.04	6.62	4

97V6

Hygroscopicity: Slowly decomposed by water with the liberation of O<sub>2</sub>.

Caution: Keep in tightly closed container.

Critical R.H.:

96.7% at 25°C

Gain (mg./g.) at R.T. after equilibrium has been established in a vacuum desiccator of a purified sample.

29  
32

31% R.H.	43% R.H.	52% R.H.	65% R.H.
24 hr. equil.	24 hr. equil.	24 hr. equil.	24 hr. equil.
3.4 4.5	0.6 2.2	2.3 21.4	84.3 178.3 56.3 136.0
75% R.H.	86% R.H.	93% R.H.	
24 hr. equil.	24 hr. equil.	24 hr. equil.	
210.5 474.7 161.0 356.0	418.4 S 251.0 682.0	S S 354.0 334.0	

Solubility Data: In water (g./100 ml.) at 20°: 0.008, in hot H<sub>2</sub>O, decomposes. Very slightly soluble in alcohol and NH<sub>4</sub>Cl. Insoluble in acetone.

Health Hazard: May cause injury on contact with skin or mucous membranes.

Safety Classifications:

OSM: Class 1. Class 2 when not stored or packed in original shipping containers or equivalent.

ICC: Listed under "Explosives and Other Dangerous Articles." Classed as oxidizing material; yellow label.

**Strontium Peroxide,  $\text{SrO}_2$  (page 3)**

**Fire and Explosion Hazard:** Heat, shock, or catalysts may cause violent decomposition. Reacts violently when heated with reducing materials. Contact with water produces heat. 12, 14

**Electrostatic Sensitivity:** —

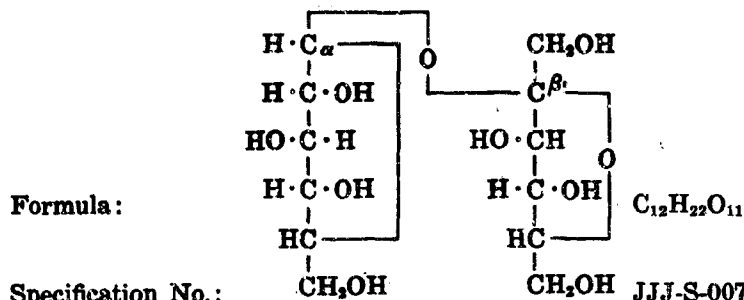
**Use in Pyrotechnics:** As an oxidizer to impart a red color to burning compositions. 17

**Additional References:**

- 1) "Direct Oxidation under High Pressures. The Oxides of Strontium, Barium, Lead, Manganese and Cobalt," C. B. Holtermann, *Ann. Chim.* 14, 121 (1940). C.A. 35, 7859 (1941)
- 2) "On the Formation and Dissociation of Strontium Peroxide," C. Holtermann and P. Lafitte, *Compt. rend.* 208, 517 (1939). C.A. 33, 2833 (1939)
- 3) "Heating Curves for the Hydrates of the Peroxides of Group II Metals," I. I. Vol'nov, C.A. 52, 19384 (1958)
- 4) "Thermography of Peroxide Compounds," I. I. Vol'nov, C.A. 48, 7416 (1954)

# SUGAR

(Cane Sugar, Sucrose, Saccharose,  
( $\alpha$ -D-glucosido)- $\beta$ -D-fructofuranoside  
 $\alpha$ -D-glucopyranosido- $\beta$ -D-fructofuranoside)



The specification covers two types of beet or cane sugar. Type 1: white, hard, refined (a) granulated or (b) powdered; and Type 2: brown, soft (a) light (b) medium and (c) dark. Type 1 granulated is used for pyrotechnics.

Molecular Weight: 342.30  
Crystalline Form: needles (from alcohol), monoclinic

For crystallography see Addnl. Ref. 3  
Sucrose crystals are triboluminescent.

Color: white  
Density, g./ml. at 15°C: crystallized, 1.5879  
powdered, 1.5897

Coefficient of Thermal Expansion, linear for

longest axis:  $28 \times 10^{-4}$   
width:  $50 \times 10^{-4}$   
shortest:  $29 \times 10^{-4}$   
cubical (calculated):  $1.1 \times 10^{-4}$

Heat of Formation, Kcal./mole at 18°C:  $H_f = -586.5$   
 $H_c = -527$

Free Energy of Formation:

Entropy, cal./deg./mole at 298°K: 86.1

Melting Point (when crystallized from alcohol): 461°K (188°C, decomp.)  
458 (185-6°C)

When sucrose is heated cautiously to the melting point (185-186°C) it forms a viscous, colorless melt; however, when heated longer or to a higher temperature decomposition takes place.

Heat of Fusion, Kcal./mole: (decomposes) 4.6

Refs.

1

29

Addnl. Ref. 5

1, 29

1

Addnl. Ref.  
3V1

Addnl. Ref.  
3V1

Addnl. Ref. 1

Addnl. Ref.  
3V1

1  
Addnl. Ref.  
3V1

Addnl. Ref.  
3V1

**Sugar (page 2)**

Boiling Point: decomposes  
 Transition Point: —  
 Heat of Sublimation: —  
 Heat Content or Enthalpy: —  
 Heat Capacity: —

**Molar Heat and Specific Heat of Crystallized Sucrose:**

Temp. °C	0	20	40	60	80	90
C <sub>p</sub> (cal./mole)	92.1	99.8	108	116	125	129
C <sub>p</sub> (cal./g.)	0.260	0.290	0.316	0.339	0.366	0.377

Addnl. Ref.  
8V1

Decomposition Temperature, °C: 160-186  
 Decomposition Products: Loses water, caramelizes, and then chars when heated above its melting point.

29  
29, 50

For DTA see Addnl. Ref. 4

Vapor Pressure: —

**X-Ray Crystallographic Data:**

System	Space Group	a	b	c	Axial Angle	Molecules/ Unit Cell
monoclinic	C <sub>2</sub>	10.89	8.69	7.77	108°	2

18  
85

Hygroscopicity: Powdered sugar absorbs up to 1% moisture in air, which is given up on heating at 90°C.

29

**Solubility of Sucrose in Water:**

Temp. °C	0	20	40	60	80	90	100
g./100 g. H <sub>2</sub> O	179.2	208.9	238.1	287.3	362.2	415.7	487.2

Solubility: In alcohol and methanol ca. 1g./100 ml. Moderate sol glycerol and pyridine. Sol ether common organic solvents. Insoluble in gasoline, CHCl<sub>3</sub>, CCl<sub>4</sub>, turpentine. Noticeably soluble in aniline, ethyl acetate, and amyl acetate.

1  
29  
Addnl. Ref. 8  
98

Health Hazard: nontoxic

Safety Classification: not listed

Fire and Explosion Hazard,  
Autoignition Temperature, °C: 385

71

Electrostatic Sensitivity: —

Specific Heat, cal./15°g./°C at 20°C: 0.299

1

Optical Rotation:  $\alpha_{\text{D}}^{25}$  (25 g. in 100 ml. H<sub>2</sub>O, 2 dm tube) + 66.47 to 66.49 depending on the solvent from which it is crystallized.

29

Heat of Combustion, Kcal./mole: 1351.8  
Kcal./g.: 3.949

Addnl. Ref. 8

Use in Pyrotechnics: as a fuel

50



**Sugar (page 3)**

**Additional References:**

- 1) L. Médard, *Mém artillerie franç* 28, 481 (1954)
- 2) "On Saccharose B," A. Pictet and H. Vogel, *Helv. Chim. Acta* 11, 901 (1928)
- 3) "Principles of Sugar Technology," P. Honig, Ed., Vol. 1, Elsevier Publishing Co., New York (1953)
- 4) "Differential Thermal Analysis of Organic Compounds," A. T. Perkins and H. L. Mitchell, *Transactions of The Kansas Academy of Science* 60, No. 4 pp. 437-40 (1957)
- 5) "X-Ray Examination of Sucrose," C. A. Beeves and W. Cochran, *Nature* 157, 872 (1946)

# **SULFUR (SULPHUR), S<sub>8</sub>** (Flowers of Sulfur, Milk of Sulfur, Brimstone)

Specification No.: JAN-S-487

The specification covers five grades of ground S:

- A, ground crude S used for black powder.
- B, ground crude S used for pyrotechnics compositions.
- C, ground crude S used for pyrotechnics compositions.
- D, ground refined S used for nongaseous powders and primer compositions.

E, ground crude S used for pyrotechnic compositions. The grades differ slightly in purity and in granulation.

Molecular Weight: 256.53

Crystalline Form: (α) rhombic, (β) monoclinic, (γ) amorphous

Color: yellow

**Forms of Sulfur:** Solid sulfur (S) exists in two crystalline forms, rhombic and monoclinic, and also as an elastomer. The rhombic form is stable at ordinary temperatures. Above the transition temperature of 95.4°C and up to the boiling point monoclinic S is the stable variety. Elastic S is prepared by rapidly chilling liquid S which has been heated to elevated temperatures. The infrared spectrum is identical with that of liquid S. On melting, S becomes a straw-yellow transparent liquid, designated as λ S. The liquid may be supercooled in bulk far below its freezing point to room temperature in the form of droplets which in time may solidify to a clear yellow glass. At about 160°C, the liquid is dark brown. Its color deepens as the temperature is raised, and above 250°C, it turns brownish-black. Apparently the structure of the liquid undergoes an abrupt change at about 160°, and this transformation is accompanied by the absorption of 2.751 cal./g. The sudden and enormous increase in viscosity which occurs at this temperature is one indication of a structural alteration. Other properties show a marked discontinuity. Long chain polymers referred to as μ S, in equilibrium with rings of octatomic molecules, apparently exist in the liquid above 160°. Beyond 230° the viscosity decreases but the color remains dark up to the boiling point, 444.6°C. If S at the boiling point is cooled slowly, it passes through the changes described above in the reverse order.

"Flowers" of sulfur is a term applied to the mined molten S which is finely ground. It is the type used for pyrotechnic purposes.

Density, g./ml.: (solid) rhombic 2.07  
monoclinic 1.96  
amorphous 1.92

Coefficient of Thermal Expansion:

Temp. °C	Linear (rhombic)	Cubic (rhombic)
0-13	$4.567 \times 10^{-6}$	$13.70 \times 10^{-6}$
13-50	$7.433 \times 10^{-6}$	$22.30 \times 10^{-6}$
50-78	$8.633 \times 10^{-6}$	$25.90 \times 10^{-6}$
78-97	$20.67 \times 10^{-6}$	$62.01 \times 10^{-6}$
97-110	$103.2 \times 10^{-6}$	$309.3 \times 10^{-6}$

Refs.

1, 46

46

20V3

1, 46

46

Sulfur (Sulphur) S<sub>8</sub> (page 2)

Heat of Formation, Kcal./mole at 298°K:	(gas) 53.25	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 43.57	9
Entropy, cal./deg./mole at 298°K:	(rhombic) 7.62	5, 9
	(monoclinic) 7.78	5, 9
See Tables a, b, c, d		
Melting Point, °C: (α) 112.8 (β) 119.25 (γ) about 120		1
Heat of Fusion, cal./g.:	(rhombic) 11.9	9
	(monoclinic) 9.2	
Boiling Point, °C:	444.6	1, 46
Heat of Vaporization, cal./mole at 717.75°K:	2300	5
Transition Point, °C:		
(rhombic → monoclinic)	95.4	46
(liquid → viscous)	159.9	46
Heat of Transition, cal./g.:		
(rhombic to monoclinic)	2.992	46
(liquid to viscous)	2.751	
Heat of Sublimation, cal./mole at 298°K:	S <sub>8</sub> 24,350	5
	S <sub>2</sub> 330,840	
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 1053	5
See Tables a, b, c, and d		

a. HEAT CONTENT AND ENTROPY OF S (c, l)  
(Base, rh-crystals at 298.15°K)

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
350 . . . . .	290	0.30
368.6 (rh) . . . . .	400	1.20
368.6 (mon) . . . . .	485	1.43
392 (mon) . . . . .	630	1.82
392 (l) . . . . .	965	2.67
400 . . . . .	1030	2.83
500 . . . . .	1940	4.85
600 . . . . .	2780	6.38
700 . . . . .	3650	7.72
717.8 . . . . .	3810	7.95

S (rh):  
Enthalpy:  $H_T - H_{298.15} = 3.58T + 3.12 \times 10^{-5}T^2 - 1345$  (0.2 percent; 298–368.6°K)

Heat Capacity:  $C_p = 3.58 + 6.24 \times 10^{-5}T$ ;  $\Delta H_{368.6} = 85$

S (mon):  
Enthalpy:  $H_T - H_{298.15} = 6.20T - 1800$  (0.1 percent; 368.6–392°K)

Heat Capacity:  $C_p = 6.20$ ;  $\Delta H_{392}$  (fusion) = 335

S (l):  
Enthalpy:  $H_T - H_{298.15} = 8.73T - 2457$  (0.6 percent; 392–717.8°K)

Heat Capacity:  $C_p = 8.73$

b. HEAT CONTENT AND ENTROPY OF S (g)  
(Base, ideal gas at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400	570	1.65	1900	8320	9.79
500	1120	2.88	2000	8830	10.06
600	1660	3.86	2200	9850	10.54
700	2190	4.68	2400	10,875	10.99
800	2715	5.38	2600	11,910	11.40
900	3235	5.99	2800	12,950	11.79
1000	3750	6.52	3000	13,995	12.15
1100	4260	7.02	3500	16,650	12.96
1200	4770	7.46	4000	19,340	13.68
1300	5280	7.87	4500	22,065	14.32
1400	5790	8.25	5000	24,810	14.90
1500	6295	8.60	5500	30,330	15.91
1600	6800	8.92	7000	35,860	16.76
1700	7305	9.23	8000	41,390	17.50
1800	7815	9.52			

S (g) :

Enthalpy:  $H_T - H_{298.15} = 5.26T - 0.05 \times 10^{-5}T^2 - 0.36 \times 10^5T^{-1} - 1443$   
(0.6 percent; 298-2400°K)Heat Capacity:  $C_p = 5.26 - 0.10 \times 10^{-5}T + 0.36 \times 10^5T^{-2}$ Enthalpy:  $H_T - H_{298.15} = 4.96T + 0.05 \times 10^{-5}T^2 - 0.60 \times 10^5T^{-1} - 1282$   
(0.2 percent; 2400-8000°K)Heat Capacity:  $C_p = 4.96 + 0.10 \times 10^{-5}T + 0.60 \times 10^5T^{-2}$ c. HEAT CONTENT AND ENTROPY OF S<sub>2</sub>(g)  
(Base, ideal gas at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400	810	2.34	1500	10,430	13.79
500	1640	4.18	1600	11,325	14.97
600	2485	5.72	1700	12,225	14.91
700	3345	7.05	1800	13,125	15.43
800	4220	8.22	1900	14,025	15.92
900	5095	9.25	2000	14,925	16.38
1000	5975	10.17	2200	16,730	17.24
1100	6855	11.01	2400	18,545	18.03
1200	7745	11.79	2600	20,360	18.76
1300	8635	12.50	2800	22,175	19.43
1400	9535	13.17	3000	23,995	20.06

Sulfur (Sulphur) S<sub>8</sub> (page 4)S<sub>8</sub>(g):Enthalpy:  $H_T - H_{298.15} = 8.72T + 0.06 \times 10^{-5}T^2 + 0.90 \times 10^{-8}T^3 - 2909$   
(0.3 percent; 298-3000°K)Heat Capacity:  $C_p = 8.72 + 0.16 \times 10^{-5}T - 0.90 \times 10^{-8}T^2$ d, HEAT CONTENT AND ENTROPY OF S<sub>8</sub>(g)  
(Base, ideal gas at 298.15°K)

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	3935	11.32	800 . . . . .	20,580	40.06
500 . . . . .	7985	20.37	900 . . . . .	24,850	45.09
600 . . . . .	12,125	27.90	1000 . . . . .	29,140	49.62
700 . . . . .	16,830	34.39			

S<sub>8</sub>(g):Enthalpy:  $H_T - H_{298.15} = 42.54T + 0.52 \times 10^{-5}T^2 + 5.04 \times 10^{-8}T^3 - 14,420$   
(0.1 percent; 298-1000°K)Heat Capacity:  $C_p = 42.54 + 1.04 \times 10^{-5}T - 5.04 \times 10^{-8}T^2$ 

Decomposition Temperature: For DTA see Addnl. Ref. 5

Decomposition Products: —

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	183.8	243.8	288.3	327.2	399.5	444.6	112.8

Form	Range	Equation (P in mm., T in °K)
rhombic	20-80	$\log P = 11.664 - \frac{5166}{T}$
monoclinic	96-116	$\log P = 11.234 - \frac{5082}{T}$
liquid	25-74	$\log P = 8.70 - \frac{4055}{T}$
	120-325	$\log P = 14.7000 - \frac{0.0062233T}{T} - \frac{6405.1}{T}$
	325-550	$\log P = 7.43287 - \frac{3268.2}{T}$

## X-Ray Crystallographic Data:

System	Space Group	a	b	c	Atoms/ Unit Cell
rhombic	V <sub>h</sub> <sup>h</sup>	10.37	12.845	24.369	128 (16 eight-membered rings)
monoclinic	C <sub>2h</sub>	10.90	10.96	11.02	48 (6 eight-membered rings)

## Hygroscopicity:

Spec. grade, % gain at 70°F in 168 h.:

none at 40, 50, and  
70% R.I.  
0.01 at 90% R.I.

**Sulfur (Sulphur) S<sub>8</sub> (page 5)**

**Solubility Data:**

In water:	insoluble	20
In alcohol and ether:	slightly soluble	
In carbon disulphide, 70 g./100 g.:	soluble	
In light petroleum, hot benzene, toluene and benzyl chloride:	soluble	46

**Health Hazard:** Believed to be nontoxic. Tank car shipments of molten sulfur may accumulate poisonous H<sub>2</sub>S gas, which is also flammable and explosive. In unloading operations suitable precautions should be taken. 93, 46

**Safety Classifications:**

OSM:	not specified
Probably class 2 as a pyrotechnic material.	
ICC:	not mentioned
U.N.	an inflammable solid
Coast Guard:	hazardous

**Fire and Explosion Hazard:** When ignited, molten S will burn in air producing acrid fumes of SO<sub>2</sub>, which are irritating, suffocating and lachrymatory. and inhalation should be avoided. Burning S can react vigorously with oxidizing materials. Sulfur when compounded with chlorates and some other oxidizing agents, forms sensitive explosive mixtures. When mixed with carbon, lampblack, fats and oils, S forms mixtures which can ignite spontaneously. It should be stored away from oxidizing agents. To fight fire use water. 12, 14, 46, 75

**Electrostatic Sensitivity:** When rubbed with most substances it becomes negatively charged.

Minimum energy required for ignition by an electric spark, millijoules: 26  
15

**Ignition Temperature, in air at atmospheric pressure, °C:** 46  
248-261  
closed cup: 405°F 75  
open cup: 440°F

**Minimum Explosive Concentration of dust, mg./l.:** 26  
35  
30 22

**Heat of Combustion, Kcal./g.:** (monoclinic) 2.240 1  
(rhombic) 2.200

**Additional References:**

- 1) "The Sulphur Data Book," W. N. Tuller, Ed., McGraw-Hill Book Co., New York (1954)
- 2) "The National Fire Codes, Vol. II, Combustible Solids, Dusts, Chemicals and Explosives," National Fire Protection Association, Inc., Boston, Mass. (1958)
- 3) "The National Fire Codes, Vol. II, The Prevention of Dust Explosions." National Fire Protection Association, Inc., Boston, Mass. (1952)
- 4) "Sulfur May Have Helical Structure," C & EN, p. 44 (Sept. 5, 1960)
- 5) Trans. Faraday Soc. 55, No. 444, 2221 (1959)

**TETRANITROCARBAZOLE, (C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>4</sub>NH**  
(Tetranitrobenzopyrrole, Tetranitroidiphenylamine, TNC)

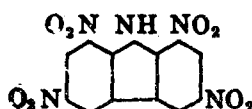
Specification No.: PAPD-639 (1954) pending revision of MIL-T-13723

Molecular Weight: 347.20

Crystalline Forms:  $\alpha$ , needles;  $\beta$ , plates;  $\gamma$  (1,3,6,8) prisms

Color: light yellow

TNC is produced by treating carbazole with sulphuric acid and then nitrating the sulphonic acids to yield a mixture of principally 1,3,6,8 and about 10% of 1,2,6,8 TNC. The structure of the 1,3,6,8 isomer is



Density, g./ml.: ———

Coefficient of Thermal Expansion: ———

Heat of Formation: ———

Free Energy of Formation: ———

Entropy: ———

Melting Point,

$\alpha$ : about 581°K (303°C) with decomposition  
 $\beta$ : 593°K (320°C)  
 $\gamma$ : (1,3,6,8) 558°K (285°C) with decomposition

Specification: 285°C min. to 300°C max.

Boiling Point: ———

Transition Point: ———

Heat of Sublimation: ———

Heat Content or Enthalpy: ———

Heat Capacity: ———

Decomposition Temperature: Decomposes on heating:

turns red-brown above 200°C

For DTA see Ref. 38

Decomposition Products: ———

Vapor Pressure: ———

X-Ray Crystallographic Data: ———

Hygroscopicity, at 30°C, 90% R.H.:

0.01

Refs.

13

13

88V20

Addnl. Ref. 1

88V20

Addnl. Ref. 5

13

**Tetranitrocarbazole, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>4</sub>NH (page 2)**

<b>Solubility Data:</b> In water (g./100 g.) at 25°C:	0.1	18, Addnl. Ref. 3
In nitrobenzene:	very soluble	
In hot acetone and hot pyridine:	soluble	
In nitrobenzene, chloroform, CCl <sub>4</sub> , ether, ligroin:	insoluble	
α—in glacial acetic acid:	practically insoluble	88V20, Addnl. Ref. 2
in KOH:	soluble with formation of a yellow color	
in conc. H <sub>2</sub> SO <sub>4</sub> :	soluble with formation of a green color	
β—in glacial acetic acid (hot):	soluble	
γ—in glacial acetic acid:	8.05%	
in pyridine:	8.55%	
in ethyl alcohol:	trace	
<b>Health Hazard:</b>	toxic; and is used as an insecticide	12
<b>Safety Classifications:</b>		
OSM:	class 9	
ICC:	not listed	
<b>Fire and Explosion Hazard:</b> Dangerous, exploded by shock. When heated to decomposition it emits highly toxic fumes. Can react vigorously with oxidizing materials.		12
<b>Electrostatic Sensitivity:</b>	—	
<b>Data on γ (1,3,6,8) TNC</b>		18
Oxygen Balance to CO <sub>2</sub> , %:	-35	
Oxygen Balance to CO, %:	-30	
Nitrogen (calc'd for C.P.) %:	20.0	
Nitro nitrogen (calc'd for C.P.) %:	16.0 (spec. min. 15.5)	
M.P., °C:	286	
<b>Impact Sensitivity:</b> 2 kg. wt., sample weight 14 mg.:		
B.M. apparatus, cm.:	100+	18
P.A., in.:	18	
<b>Friction Pendulum Test:</b>	unaffected by fibre or steel shoe	
<b>Explosion Temperature (5 sec.), °C:</b>	decomposes at 470	
<b>100°C Heat Test:</b>		
% loss first 48 hrs.:	0.15	
% loss second 48 hrs.:	0.05	
Explosion in 100 hrs.:	none	
<b>Vacuum Stability Test, cc. gas/40 hrs. from a 5 g. sample:</b>		
100°C:	0.2	
120°C:	0.2	
<b>Sand Test (200 g. bomb)</b>		
Sand crushed through 80 mesh screen:	(gas) 41.3	



**Tetranitrocarbazole,  $(C_6H_7)_2(NO_2)_4NH$  (page 3)**

Sensitivity to Initiation:

Lead Azide 0.20 g. plus tetryl 0.25 g.

Method of Loading:

pressed

Method of Storage:

dry

Heat of Combustion, cal./g. at 18°C:

3772.4

Use in Pyrotechnics:

as a fuel, particularly in  
some igniter powders

Addnl. Ref. 3

**Additional References:**

- 1) "Identification of Isomers Formed in the Nitration of Carbazole," D. B. Murphy et al., *J. Am. Chem. Soc.* **75**, 4239 (1953)
- 2) *C.A.* **48**, 2084 (1954)
- 3) Picattiny Arsenal Technical Reports 1647, 1802, 1937, 1973, 1984, and 2180
- 4) P. Tavernier and Maurice Lamoroux, *Mem. Poudres* **39**, 341 (1957)
- 5) "Über die Einwirkung von Athylnitrat auf Diphenyl und Diphenyl. Abkömmlinge," H. Raudnitz, *Ber.* **60**, 741 (1927)

## "THIOKOL" (LIQUID POLYMER LP-2)

(Thiokol is a trademarked name)

Thiokol LP-2 Mix is a polymer manufactured by the Thiokol Corporation in the liquid state. It is a completely polymerizable material which can be converted by suitable curatives to a tough resilient rubber without appreciable shrinkage. In the rubber state it remains flexible to -65°F and does not melt at elevated temperatures. Its maximum service temperature is around 250°F, but it will stand higher intermittent temperatures. It is sold as a viscous liquid with a viscosity of about 400 poises at 25°C. It is cold setting.

Formula or Structure: The average structure is as follows:

$\text{HS}-(\text{C}_2\text{H}_4-\text{CH}_2-\text{O}-\text{C}_2\text{H}_4-\text{S}-\text{S})_n-\text{C}_2\text{H}_4-\text{O}-\text{CH}_2-\text{O}-\text{C}_2\text{H}_4-\text{SH}$ . Occasionally in the chain of recurring units there is a side mercaptan group. The terminal SH groups are very reactive.

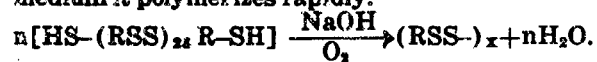
Specifications:

none

Physical Properties:

Color: amber  
Specific Gravity: 1.27  
Molecular Weight: approximately 4000  
Stability: indefinite  
Moisture Control: less than 0.2%  
pH (of water extract): 6.0 to 8.0

Chemical Reactivity: LP-2 is slightly acid when pure and is stable. In alkaline medium it polymerizes rapidly.



The reaction is exothermic. R in the above equation denotes the group  $(\text{C}_2\text{H}_4-\text{O}-\text{CH}_2-\text{O}-\text{C}_2\text{H}_4)$ .

Curing: Organic peroxides; e.g., benzoyl peroxide, tertiary butylhydroperoxide, tertiary butylbenzoate, and cumene hydroperoxide will promote cure. Conventional paint driers will serve to introduce O from the air and can be used to polymerize LP-2. Cobalt driers are outstanding for this purpose.

Compatibility Data:

In the data given below solutions were prepared by stirring small increments of solvent into weighed quantities of the liquid polymer and continuing until precipitation or cloudiness occurred. The figures given indicate the ultimate tolerance of LP-2 for the solvent. Thus 70% for methylethyl ketone indicates 70% of the ketone and 30% LP-2 by weight. At 100%, dilution is infinite.

Solvent	%	Solvent	%
glacial acetic acid	20	cyclohexanone	100
methanol	0	aniline	10
ethanol	0	benzene	100
diethyl ether	20	toluene	100
dioxane	100	carbon tetrachloride	70
petroleum ether	10	ethyl acetate	100
acetone	50	dibutylphthalate	100
methylethylketone	70	nitromethane	60

These figures do not hold for polymerized LP-2 which has low solubility.

Use in Pyrotechnics: As a fuel when polymerized

Refs.

All data from  
Thiokol  
Corporation,  
Trenton, N.J.,  
Ref. 59

# TITANIUM, Ti

Refs.

Specification No.:	MIL-T-13405A (CmlC)	
Molecular Weight:	47.90	
Crystalline Form (at temperatures up to about 800°C):	$\alpha$ , hexagonal $\beta$ , cubic	1
Color:	silver grey to dark grey	1
Density, g./ml.:	(solid) 4.50	
Coefficient of Thermal Expansion, linear ( $\alpha$ ), at R.T.:	$8 \times 10^{-6}$	38
Temp. Range °C	Coefficient	27
-195 to +20	$6.8 \times 10^{-6}$	
20-200	$8.9 \times 10^{-6}$	
20-400	$9.9 \times 10^{-6}$	
20-800	$10.1 \times 10^{-6}$	
Heat of Formation, Kcal./mole at 298°K:	(gas) 112.6	5
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 101.944	5
Entropy, cal./deg./mole at 298°K:	(c) 7.33 (gas) 43.07	2, 5 1, 5
See Tables a and b		
Melting Point:	1940°K (1667°C)	4
Heat of Fusion, cal./mole:	8700	5
Boiling Point:	3550°K (3277°C)	5
Heat of Vaporization, cal./mole:	102,500	5
Transition Point, hexagonal ( $\alpha$ ) to cubic ( $\beta$ ):	1155°K (882°C)	4, 5, 9
Heat of Transition, cal./mole:	950	4
Heat of Sublimation, cal./mole at 298°K:	112,600	5
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 1150 (gas) 1802	5
See Tables a and b		

## a. HEAT CONTENT AND ENTROPY OF Ti (c, l) (Base, $\alpha$ -crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	625	1.80	1500	9600	12.05
500	1250	3.20	1600	10,350	12.53
600	1920	4.42	1700	11,100	12.99
700	2610	5.48	1800	11,850	13.42
800	3330	6.44	1900	12,600	13.82
900	4070	7.31	1940 ( $\beta$ )	12,900	13.98
1000	4840	8.12	1940 (l)	17,360	16.28
1100	5630	8.87	2000	17,840	16.52
1155 ( $\alpha$ )	6070	9.26	2200	19,440	17.29
1155 ( $\beta$ )	7020	10.09	2400	21,040	17.98
1200	7350	10.33	2600	22,640	18.62
1300	8100	10.98	2800	24,240	19.21
1400	8850	11.53	3000	25,840	19.77

Titanium, Ti (page 2)

Ti (α):

Enthalpy:  $H_T - H_{298.15} = 5.25T + 1.28 \times 10^{-5}T^2 - 1677$  (0.3 percent; 298-1155°K)

Heat Capacity:  $C_p = 5.25 + 2.52 \times 10^{-5}T$

Ti (β):

Enthalpy:  $H_T - H_{298.15} = 7.50T - 1650$  (0.1 percent; 1155-1940°K)

$\Delta H_{\text{fusion}} = 4450$

Ti (l):

Enthalpy:  $H_T - H_{298.15} = 8.00T + 1840$  (0.1 percent; 1940-3000°K)

b. HEAT CONTENT AND ENTROPY OF Ti (g)  
(Case, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	575	1.67	1900	8495	9.87
500	1120	2.88	2000	9075	10.16
600	1650	3.84	2200	10,275	10.74
700	2170	4.64	2400	11,530	11.28
800	2685	5.28	2600	12,840	11.79
900	3195	5.94	2800	14,210	12.31
1000	3705	6.47	3000	15,635	12.81
1100	4215	6.96	3500	19,460	13.98
1200	4730	7.40	4000	23,630	15.16
1300	5245	7.82	4500	28,110	16.15
1400	5765	8.20	5000	32,955	17.15
1500	6290	8.57	6000	42,895	18.98
1600	6825	8.91	7000	53,320	20.59
1700	7370	9.24	8000	63,830	21.99
1800	7930	9.56			

(g):

Enthalpy:  $H_T - H_{298.15} = 4.72T + 0.20 \times 10^{-5}T^2 - 0.90 \times 10^{-7}T^3 - 1123$   
(0.3 percent; 298-2000°K)

Heat Capacity:  $C_p = 4.72 + 0.40 \times 10^{-5}T + 0.30 \times 10^{-7}T^2$

Enthalpy:  $H_T - H_{298.15} = 3.72T + 0.59 \times 10^{-5}T^2 - 1.58 \times 10^{-7}T^3 - 682$   
(0.6 percent; 2000-6000°K)

Heat Capacity:  $C_p = 3.72 + 1.18 \times 10^{-5}T - 1.58 \times 10^{-7}T^2$

Heat Capacity, cal./mole at 298°K: (solid) (β) 7.50  
(liquid) 8.00  
(gas) 5.84

E, 9

See also above

Decomposition Temperature: \_\_\_\_\_

Decomposition Products: \_\_\_\_\_

Vapor Pressure: In the temp. range 1650-1810°K;  $\log p = 7.80 - \frac{24200}{T}$

28

$p$  = press. in atmospheres and  $T$  = absolute temp.

For other equations see Ref. 88 and Addnl. Refs. 3 and 4

**Titanium, Ti (page 3)**

**X-Ray Crystallographic Data.**

System	Space Group	a	c	Atoms/Unit Cell
hexagonal	D <sub>6h</sub>	2.951	4.692	2
cubic		3.288		2

**Hygroscopicity (cumulative increase in weight after)**

Storage over H<sub>2</sub>O for 29 days: 1.7%

H<sub>2</sub>SO<sub>4</sub> for 29 days: 0.0%

Two days in oven at 105°C: 0.0%

**Solubility Data: In cold water:**

insoluble

In hot water:

decomposes

In dilute acids on heating:

soluble

**Health Hazard:**

none; physiologically inert

**Safety Classifications:**

GSM:

class 2

ICC: Powder listed under "Explosives and Other Dangerous Articles" as a flammable solid; yellow label.

U.N.:

flammable solid

**Fire and Explosion Hazard:** Powdered metal exposed to air is a dangerous fire hazard and burns with intense heat. Prevent water from contacting the material. Store and process in rooms or buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction of powdered metal and moisture. When mixed with oxidizing material, the powdered metal is a dangerous fire and explosion hazard. In the repair and maintenance of buildings or equipment, powder or dust should be removed and nonsparking tools used.

Finely ground titanium powder explodes spontaneously when in contact with hot air, and burns in atmospheres other than air. At 680°C, the fine powder burns in pure carbon dioxide. At red heat, titanium decomposes steam to free hydrogen. Above 1475°F it burns vigorously in atmosphere of pure nitrogen. The metal and its alloys explode when treated with nitric acid. Oil covered titanium chips have ignited spontaneously.

**Precautions When Handling Titanium:**

Titanium powder is shipped and stored wet. Moisture content of containers of titanium powder should be kept above 20% by volume. All standard precautions must be taken when handling the powder. Metal equipment with which it comes in contact must be grounded, and operations carried out in atmospheres of helium, or argon. Atmospheres of carbon dioxide and nitrogen are ineffective since dust layers of the powder ignite in these gases.

**Electrostatic Sensitivity (minimum energy required for ignition of powder by electric sparks, millijoules):**

(dust cloud) 10

(dust layer) .008

**Ignition Temperature, °C:**

Massive metal in air

700-800

Powder in air

250

Dust Cloud

380

Dust Layer

380

**Titanium, Ti (page 4)**

**Minimum Explosive Concentration:**

Powdered metal, mg./l. 45

26

**Corrosion Resistance:** Extremely resistant to corrosion by most substances.

38

**Use in Pyrotechnics:** As a fuel. According to the specification, it is used in first fire mixtures for incendiary munitions.

**Additional References:**

- 1) "The Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium and Their Hydrides," I. Hartmann et al., Bureau of Mines R.I. 4835 (1951)
- 2) Ref. 64
- 3) L. G. Carpenter, *Nature* 163, 527 (1949)
- 4) *J. Phys. Chem.* 59, 127-131 (1955)

TITANIUM DIOXIDE, $\text{TiO}_2$ (Titanis, Titanium White, Rutile, Anatase, Brookite)		Refs.
Percent Oxygen:	40.08	1, 29
Specification No.:	TT-2-25a (Dry-Paint Pigment)	
The specification covers one grade and three types of titanium dioxide pigment which vary in purity:		
Type I, Free chalking (anatase)		
II, Semi-chalking, aluminum treated (rutile)		
III, Chalk-resisting, silicon-aluminum-zinc-treated (rutile)		
Molecular Weight:	79.90	
Crystalline Form:	tetragonal	1
Allotropic Forms: $\text{TiO}_2$ occurs in four allotropic forms; brookite, rutile, and two forms of anatase. The stability fields of these modifications have not been clearly determined, but anatase II is reported to transform to anatase I at $642^\circ\text{C}$ , and anatase I to rutile at $915^\circ\text{C}$ . The first transformation is rapid; the second slow. The formation of a rutile structure also has been found to occur when $\text{Ti}_2\text{O}_3$ is oxidized.		65
Color: (purified titania) translucent water white or yellowish cast. Turns yellow then brown when heated.		29 54V7
Density, g./ml.:	(solid) brookite 4.17 octahedrite, anatase, 3.84 rutile 4.26	1 1, 22 1
Coefficient of Thermal Expansion:	$9 \times 10^{-6}$	41
Ref. quotes Addnl. Ref. 5		
Coefficient of Thermal Expansion per $^\circ\text{C}$ :	$(E \times 10^{-7})$ where E is 70-80 over the range 20-600 $^\circ\text{C}$	Addnl. Ref. 4
Heat of Formation, Kcal./mole at $298^\circ\text{K}$ :	(c, III) rutile, -218.0	1, 9
See Table a		
Free Energy of Formation, Kcal./mole at $298^\circ\text{K}$ :	(c, III) rutile, -203.8	
See Table a		
a. HEAT AND FREE ENERGY OF FORMATION OF $\text{TiO}_2$ (rutile)		2

T, $^\circ\text{K}$	$\Delta H$ (cal./mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . . .	-225,500 ( $\pm 250$ )	-212,300 ( $\pm 250$ )
400 . . . . .	-225,350	-207,800
500 . . . . .	-225,100	-203,450
600 . . . . .	-224,900	-199,150
700 . . . . .	-224,700	-194,850
800 . . . . .	-224,500	-190,600
900 . . . . .	-224,300	-186,400
1000 . . . . .	-224,150	-182,200
1100 . . . . .	-224,000	-178,000
1150 . . . . .	-223,950	-175,900
1150 . . . . .	-224,900	-175,900

Titanium Dioxide, TiO<sub>2</sub> (page 2)

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
1200 . . . . .	-224,800	-173,800
1300 . . . . .	-224,600	-169,550
1400 . . . . .	-224,400	-165,300
1500 . . . . .	-224,150	-161,100
1600 . . . . .	-223,900	-156,950
1700 . . . . .	-223,650	-152,750
1800 . . . . .	-223,400	-148,600
1900 . . . . .	-223,150	-144,450
2000 . . . . .	-222,850	-140,300

Free Energy Equations:

Reaction	Range of Validity, °K
1) Ti (α) + O <sub>2</sub> (g) = TiO <sub>2</sub> (rutile)	238.16-1150
Δ F <sub>T</sub> <sup>o</sup> = -228,360 - 12.80T log T + 1.62 (10 <sup>-3</sup> T <sup>2</sup> ) + 1.975 (10 <sup>5</sup> T <sup>-1</sup> ) + 82.81T	
2) Ti (β) + O <sub>2</sub> (g) = TiO <sub>2</sub> (rutile)	1150-2000
Δ F <sub>T</sub> <sup>o</sup> = -228,380 - 7.62T log T + .36 (10 <sup>-3</sup> T <sup>2</sup> ) + 1.975 (10 <sup>5</sup> T <sup>-1</sup> ) + 68.43T	

Entropy, cal./deg./mole at 298°K:

(c, III) rutile, 12.01

See Tables b, c

Melting Point:

2108°K (1835°C)

Heat of Fusion, Kcal./mole:

15.5 ± 2.5

Boiling Point:

(rutile) 2500°K (2227°C)

Heat of Vaporization, Kcal./mole:

138.9

Transition Point:

—

Heat of Sublimation:

—

b. HEAT CONTENT AND ENTROPY OF TiO<sub>2</sub>(rutile)  
(Base, crystals at 298.15°K)

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	1540	4.43	1300 . . . . .	17,000	24.38
500 . . . . .	3100	7.91	1400 . . . . .	18,820	25.73
600 . . . . .	4735	10.89	1500 . . . . .	20,680	27.00
700 . . . . .	6440	13.51	1600 . . . . .	22,530	28.20
800 . . . . .	8160	15.81	1700 . . . . .	24,420	29.55
900 . . . . .	9900	17.86	1800 . . . . .	26,340	30.44
1000 . . . . .	11,650	19.70	1900 . . . . .	28,280	31.49
1100 . . . . .	13,420	21.39	2000 . . . . .	30,250	32.56
1200 . . . . .	15,200	22.94			

TiO<sub>2</sub>(rutile):

Enthalpy: H<sub>T</sub> - H<sub>298.15</sub> = 17.97T + 0.14 × 10<sup>-3</sup>T<sup>2</sup> + 4.35 × 10<sup>5</sup>T<sup>-1</sup> - 6829  
(0.8 percent; 298-1800°K)

Heat Capacity: C<sub>p</sub> = 17.97 + 0.28 × 10<sup>-3</sup>T - 4.35 × 10<sup>5</sup>T<sup>-2</sup>



Titanium Dioxide, TiO<sub>2</sub> (page 3)

c. HEAT CONTENT AND ENTROPY OF TiO<sub>2</sub>(anatase)  
(Base, crystals at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	1540	4.43	900 . . . . .	9930	17.89
500 . . . . .	3100	7.91	1000 . . . . .	11,720	19.78
600 . . . . .	4735	10.89	1100 . . . . .	13,530	21.51
700 . . . . .	6440	13.52	1200 . . . . .	15,350	23.09
800 . . . . .	8170	15.82	1300 . . . . .	17,180	24.55

TiO<sub>2</sub>(anatase) :

Enthalpy:  $H_T - H_{298.15} = 17.83T + 0.25 \times 10^{-5}T^2 + 4.23 \times 10^5T^{-1} - 6757$   
(0.7 percent; 298-1300°K)

Heat Capacity:  $C_p = 17.83 + 0.50 \times 10^{-5}T - 4.23 \times 10^5T^{-2}$

Heat Capacity, cal./deg./mole: (solid) 13.16

9

See equations above

Decomposition Temperature: —

Decomposition Products: —

Dissociation Pressures: —

63

Vapor Pressure,  $\log p_{\text{atm.}} = -\frac{30361}{T} - 0.492 \times 10^{-5} + 11.19$  (T = °K)

Addnl. Ref. 1

at 2000°K,  $\log p = 4.97$  atm. See also Ref. 54V6

X-Ray Crystallographic Data:

1

System	Space Group	a	c	Molecules/Unit Cell
(rutile) tetragonal	D <sub>4h</sub> <sup>14</sup>	4.58	2.95	2

Hygroscopicity: nonhygroscopic

Solubility Data: In water, HCl, HNO<sub>3</sub>, dil. H<sub>2</sub>SO<sub>4</sub>: insoluble

1

In hot concentrated H<sub>2</sub>SO<sub>4</sub>, alkalis: soluble

Health Hazard: Considered harmless but high concentrations of the dust may cause irritation to the respiratory tract.

12, 25

M.A.C., mg./m.<sup>3</sup> of air: (tentative) 15

29

Safety Classifications:

OSM: not listed

ICC: not listed

Fire and Explosion Hazard: none

Electrostatic Sensitivity: —

Use in Pyrotechnics: a product of the combustion of Ti

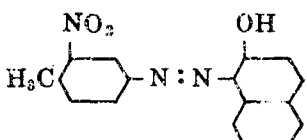
Additional References:

- 1) "Vapor-Solid Equilibria in the Titanium Oxygen System," W. Groves et al., J. Phys. Chem. 59, 127 (1955)
- 2) Ref. 64
- 3) For color changes see also Ref. 44V29 sup
- 4) F. Hummel and E. Henry, Report 6, Penn. State College School of Mineral Industries, PB 60, 659 (1946) ; cited by Ref. 65
- 5) Ind. Eng. Chem. 38, 1697 (1946)

**TOLUIDINE-RED TONER (dry paint pigment)**  
**(1-(3-Nitro-p-Tolueneazo)-2-Naphthol,**  
**Metanitroparatoluidino-azo-Betanaphthol, C.I. 12120,**  
**C.I. Pigment Red 3)**

*Refs.*

82, 48A

Formula:	$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_{10}\text{H}_6\text{OH}$ 	$\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_3$	
Specification No.:	TT-T-562		
The color shall be resistant to $\text{HNO}_3$ (1.20 Sp. Gr.), to HCL (1.10 Sp. Gr.) and to 10% caustic soda solution.			
Molecular Weight:	307.32		
Crystalline Form:	microscopic delicate feathery needles	82	
Color:	purplish or brown; bright red to somewhat darker yellowish red	82 Spec. 84A	
Density, g./ml.:	(solid) 1.40 (bulking value) 0.08576	82 82	
Coefficient of Thermal Expansion:	---		
Heat of Formation:	---		
Free Energy of Formation:	---		
Entropy:	---		
Melting Point, °C:	258	48A	
Heat of Fusion:	---		
Boiling Point:	---		
Transition Point:	---		
Heat of Sublimation:	---		
Heat Content or Enthalpy:	---		
Heat Capacity:	---		
Decomposition Temperature:	---		
Decomposition Products:	---		
Vapor Pressure:	---		
X-Ray Crystallographic Data:	---		
Hygroscopicity:	---		
Solubility Data: In acetone and chloroform:	soluble	82	
In alcohol and benzene:	slightly soluble	48A	
In hot water:	very slightly soluble	82	
Health Hazard:	---		
Safety Classifications:	---		

**Toluidine-red toner (page 2)**

**Fire and Explosion Hazard:**

—

**Electrostatic Sensitivity:**

—

**Resistance to light:**

(full shade) excellent  
(tint) good

82

to heat:

to 320°F  
poor when baked 20 min.  
at 270°F

to acids and alkalis:

good

**Use in Pyrotechnics.** Added to igniter compositions to impart a red color for identification.

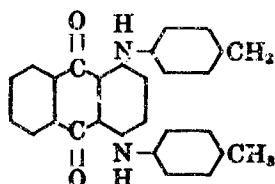
**Additional References:**

- 1) Ref. 82

**1,4-di-p-TOLUIDINOANTHRAQUINONE**  
**(1,4-di-p-tolyaminoanthraquinone,**  
**D & C Green No. 6, Quinizarine**  
**Green G Base, C.I. 61565, C.I. Solvent Green 3)**

*Refs.*  
 92, 43A

Formula:



$C_{28}H_{22}N_2O_2$

Specification No.:

MIL-D-3277

Molecular Weight:

418.5

Crystalline Form:

needles

88V14

Color: Green, from chlorobenzol—blue,  
 from glacial acetic acid—dark violet

88V14

88V14

Density, g./ml.

Apparent Density:

(Spec.)  $0.45 \pm 0.25$

Temperature Coefficient:

Heat of Formation:

Free Energy of Formation:

Entropy:

Melting Point:

491°K (218°C)

88V14

Heat of Fusion:

Boiling Point:

Transition Point:

Heat of Sublimation:

Heat Content or Enthalpy:

Heat Capacity:

Decomposition Temperature:

Decomposition Products:

Vapor Pressure:

X-Ray Crystallographic Data:

Hygroscopicity:

Solubility Data: In alcohol (g./l.) : 60°C:

34

Addnl. Ref. 1

In aniline:

soluble with green color

88V14

In concentrated  $H_2SO_4$ :

soluble with violet-blue  
 color or violet-red

In chloroform and in benzene:

soluble

Health Hazard:

unknown

92

**1,4-Di-p-toluidinoanthraquinone (page 2)**

**Safety Classification:**

OSM:

not listed

ICC:

not listed

**Fire and Explosion Hazard:**

-----

**Electrostatic Sensitivity:**

-----

**Use in Pyrotechnics:**

to color smoke mixtures  
green

**Additional References:**

- 1) "The Dyeing Phenomena of Acetate Artificial Silk," V. Kartaschoff and G. Farine, *Helv. Chim. Acta* 2, 822 (1928)

**TUNGSTEN, W**  
(Wolfram)

Refs.

Specification No.:	MIL-T-13827	
Molecular Weight:	183.86	
Crystalline Form:	(cubic) $\beta$ -form trans- forms irreversibly to $\alpha$ above 700°C	5
Color:	grey-black	1
Density, g./ml.:	(solid) 19.3	
Coefficient of Thermal Expansion, linear:		
-108 to 0°C:	$4.2 \times 10^{-6}$	1
0-100:	$4.3 \times 10^{-6}$	
0-300:	$4.5 \times 10^{-6}$	
0-500:	$4.6 \times 10^{-6}$	
1000-2000:	$6.1 \times 10^{-6}$	
Heat of Formation, cal./mole at 298°K:	(gas) -200,000	5
Free Energy of Formation, cal./mole at 298°K:	(gas) -190,009	1, 5
Entropy, cal./deg./mole at 298°K:	(gas) 41.55	5
	(c) 8.04	
See Tables b, c		
Melting Point, °K:	3650	5
Heat of Fusion, cal./mole:	8420	5, 7
Boiling Point:	5800°K (5427°C)	5
Heat of Vaporization, cal./mole:	191,000	5
Transition Point:	—	
Heat of Sublimation, cal./mole:	200,000	5
Heat Content or Enthalpy, cal./mole:	(solid) 1216	5
	(gas) 1486	
Heat Capacity:	(solid) 5.92	5
	(liquid) 8.5	
	(gas) 7.5	

**a. HEAT CAPACITY OF TUNGSTEN (solid)**

5

T, °K	$C_p$ cal./deg./mole	T, °K	$C_p$ cal./deg./mole
298 . . . . .	5.92	1600 . . . . .	7.00
600 . . . . .	6.17	2000 . . . . .	7.33
800 . . . . .	6.34	2500 . . . . .	7.74
1000 . . . . .	6.50	3000 . . . . .	8.15
1200 . . . . .	6.67		

See also equation below

b. HEAT CONTENT AND ENTROPY OF W (c)  
(Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	615	1.77	1500	7730	10.18
500	1220	3.12	1600	8430	10.63
600	1830	4.23	1700	9130	11.06
700	2450	5.19	1800	9840	11.47
800	3080	6.03	1900	10,550	11.85
900	3710	6.77	2000	11,270	12.22
1000	4360	7.46	2200	12,720	12.91
1100	5010	8.08	2400	14,190	13.55
1200	5670	8.65	2600	14,680	14.14
1300	6340	9.19	2800	17,190	14.70
1400	7030	9.70	3000	18,720	15.23

W (c) :

Enthalpy:  $H_T - H_{298.15} = 5.74T + 0.38 \times 10^{-5}T^2 - 1745$  (0.4 percent; 298-3000°K)Heat Capacity:  $C_p = 5.74 + 0.76 \times 10^{-5}T$ 

c. HEAT CONTENT AND ENTROPY OF W (g)  
(Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	540	1.55	1500	10,150	12.47
500	1130	2.56	1600	11,040	13.04
600	1805	4.09	1700	11,895	13.56
700	2580	5.28	1800	12,730	14.04
800	3440	6.44	1900	13,540	14.47
900	4375	7.53	2000	14,325	14.81
1000	5350	8.56	2200	15,855	14.83
1100	6340	9.50	2400	17,330	16.21
1200	7325	10.36	2600	18,780	16.83
1300	8200	11.14	2800	20,210	17.36
1400	9235	11.84	3000	21,635	17.35

W (g) :

Enthalpy:  $H_T - H_{298.15} = 10.70T - 0.66 \times 10^{-5}T^2 + 4.64 \times 10^{-9}T^3 - 4688$   
(0.3 percent; 1600-3000°K)Heat Capacity:  $C_p = 10.70 - 1.32 \times 10^{-5}T + 4.64 \times 10^{-9}T^2$



**Tungsten, W (page 3)**

Vapor Pressure: At 2000-3500°K can be calculated from  $\log p(\text{mm. Hg.}) = -\frac{4200}{T} + 9.84 - 0.0146 \log T - 0.164T$ . Where T = temperature °K. Vapor pressure is 1 mm. at 3990°C

**X-Ray Crystallographic Data:**

System	Space Group	a	Atoms/Unit Cell
$\alpha$ , cubic	$O_h^2$	3.1583	2
$\beta$ , cubic	$O_h^2$ or $O_h^3$	5.04	8

**Hygroscopicity:**

**Solubility Data: In water:**

In  $HNO_3$ ,  $H_2SO_4$ , and aqua regia:

In HF and  $HNO_3$ :

insoluble  
very slightly soluble  
soluble

**Health Hazard:**

very slight

**Safety Classifications:**

OSM:

class 2

**Fire and Explosion Hazard:** Tungsten is dangerous in the powdered form when exposed to flame. It burns with intense heat. Prevent water from contacting the material. Store and process only in rooms or buildings adequately vented at the highest point to prevent the accumulation of hydrogen gas which results from the reaction of the powdered metal and moisture.

When compounded with oxidizing agents, the powdered metal is a dangerous fire and explosion hazard. In the repair or maintenance of buildings or equipment, powder or dust should be removed and nonsparking tools used.

**Electrostatic Sensitivity:**

**Use in Pyrotechnics:**

as a fuel

**Additional References:**

- 1) "Tungsten," C. J. Smithells, Chapman & Hall Ltd., London (1952)
- 2) Ref. 46

# **TUNGSTEN DIOXIDE, WO<sub>2</sub>**

*Refs.*

Specification No.:	—	
Molecular Weight:	215.92	1A
Crystalline Form:	cubic	1A
Color:	brown	1A
Density, g./ml.:	(solid) 12.11	1A
Coefficient of Thermal Expansion:	—	
Heat of Formation, Kcal./mole at 298°K:	(c) -134.0 ± 2.5 -136.3	24A 1, 9, 31A
Free Energy of Formation, Kcal./mole at 298°K:	(c) -123.8 -122 -118	6 8 31A

## **HEAT AND FREE ENERGY OF FORMATION OF WO<sub>2</sub>(c)**

2

T, °K	Δ H (cal./mole)	Δ F° (cal./mole)
298.16 . . . .	-137,000 (± 2000)	-124,500 (± 2000)
400 . . . . .	-136,900	-120,400
500 . . . . .	-136,900	-116,300
600 . . . . .	-136,800	-112,100
700 . . . . .	-136,800	-108,000
800 . . . . .	-136,700	-103,900
900 . . . . .	-136,600	-99,800
1000 . . . . .	-136,600	-95,800
1100 . . . . .	-136,500	-91,700
1200 . . . . .	-136,500	-87,600
1300 . . . . .	-136,400	-83,500
1400 . . . . .	-136,300	-79,500
1500 . . . . .	-136,300	-75,400

Entropy, cal./deg./mole at 298°K:	15 15.5 16.0 ± 2.5	6 2 24A
Melting Point, °K: See Decomposition Temperature below. Ignites in air. Ignites in nitrogen at 1500–1600°C.		31A
Heat of Fusion, Kcal./mole	11.5	6
Boiling Point: Begins to sublime at about 800°C. Quite volatile above 1050°. The boiling point is about 1800°K.		44S54
Heat of Vaporization, Kcal./mole:	48.86	44S54
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature, °K:	decomposes at 2125 ± 50	8
Decomposition Products:	W + WO <sub>2</sub> which sublimes	44S54

**Tungsten Dioxide, WO<sub>2</sub> (page 2)**

Vapor Pressure:						appreciable at 1800°K	44S54
X-Ray Crystallographic Data:							
<i>System</i>	<i>Space Group</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>Axial Angle</i>	<i>Molecules/ Unit Cell</i>	
monoclinic	P <sub>21</sub>	5.65	4.89	5.55	120° 25'	4	4, 24A
tetragonal	D <sub>4h</sub>	4.86		2.77		2	2, 1A, 97
Hygroscopicity:						—	
Solubility Data: In H <sub>2</sub> O, acids, KOH:						insoluble	1A
Health Hazard:						slightly toxic	
Safety Classifications:							
OSM:						not listed	
ICC:						not listed	
Fire and Explosion Hazard: The amorphous powder is strongly pyrophoric and easily oxidized to WO <sub>3</sub> .							50V14
Electrostatic Sensitivity:						—	
Use in Pyrotechnics:						—	

# ZINC, Zn

Refs.

Specification No.:	JAN-Z-385	
Covers three grades, which differ in purity, and two classes differing in granulation.		
Molecular Weight:	65.38	
Crystalline Form:	hexagonal	1
Color:	bluish-white	1
Density, g./ml.:	(solid) 7.14	1
Coefficient of Thermal Expansion, linear at 10-100°C:	$26.28 \times 10^{-6}$	1
cubic at 0-100°C:	$89.28 \times 10^{-6}$	
Equation for linear coefficient: $\alpha_t = \alpha_0 (1 + .2969 \times 10^{-4} t + (-.0635 \times 10^{-7} t^2))$		1
where $\alpha_t$ = length at temp. $t$ in °C and $\alpha_0$ = length at 0°C		
Heat of Formation, Kcal./mole at 298°K:	(gas) 31.18	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 22.682	5
Entropy, cal./deg./mole, at 298°K:	(c) 9.95	1, 5
	(gas) 38.45	1, 5
See Tables a and b		
Melting Point:	692.7°K (419.6°C)	4, 5
Heat of Fusion, cal./mole:	1765	4, 5
Boiling Point:	1181°K (90°°C)	5
Heat of Vaporization, cal./mole:	27,560	5
Transition Point:	—	
Heat of Sublimation, cal./mole	31,166	5
Heat Content or Enthalpy, cal./mole:	(solid) 1349	5
See equations below		

## a. HEAT CONTENT AND ENTROPY OF Zn (c, l) (Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400 . . . . .	625	1.80	800 . . . . .	5156	9.08
500 . . . . .	1270	3.24	900 . . . . .	5900	9.96
600 . . . . .	1940	4.46	1000 . . . . .	6650	10.75
692.7 (c) . . . .	2580	5.45	1100 . . . . .	7400	11.47
692.7 (l) . . . .	4345	8.00	1200 . . . . .	8150	12.12
700 . . . . .	4406	8.08			

Zn (c) :

$$H_T - H_{298.15} = 5.35T + 1.20 \times 10^{-5} T^2 - 1702 \quad (0.3 \text{ percent, } 298-692.7^\circ\text{K})$$

$$\text{Heat Capacity: } C_p = 5.35 + 2.40 \times 10^{-5} T$$

Zn (l) :

$$\text{Enthalpy: } H_T - H_{298.15} = 7.50T - 850 \quad (0.1 \text{ percent; } 692.7-1200^\circ\text{K})$$

Zinc, Zn (page 2)

b. HEAT CONTENT AND ENTROPY OF Zn (g)  
(Base, ideal gas at 98.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400	505	1.46	1900	7960	9.20
500	1005	2.57	2000	8455	9.46
600	1500	3.48	2200	9450	9.93
700	1995	4.24	2400	10,445	10.36
800	2495	4.90	2600	11,440	10.76
900	2990	5.49	2800	12,435	11.13
1000	3490	6.01	3000	13,425	11.47
1100	3985	6.49	3500	15,910	12.24
1200	4480	6.92	4000	18,400	12.90
1300	4980	7.32	4500	20,905	13.49
1400	5475	7.69	5000	23,435	14.03
1500	5975	8.03	6000	28,675	14.98
1600	6470	8.35	7000	34,385	15.36
1700	6965	8.65	8000	40,905	16.73
1800	7465	8.94			

Zn (g) :

Enthalpy:  $H_T - H_{298.15} = 4.97T - 1432$  (0.1 percent; 298-5000°K)

Heat Capacity, cal./deg./mole:

(solid) 6.07  
(liquid) 7.50  
(gas) 4.97

4, 5

Also see above

Decomposition Temperature: \_\_\_\_\_

Decomposition Products: \_\_\_\_\_

Vapor Pressure: \_\_\_\_\_

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	487	593	673	736	844	907	419.4

1

X-Ray Crystallographic Data:

System	Space Group	a	c	Atoms/Unit Cell
hexagonal	D <sub>6h</sub>	2.6585	4.9342	2

Hygroscopicity: On exposure to moist air zinc becomes coated with a white basic carbonate of Zn. Cumulative increase in weight after:

16, 29

Storage over H<sub>2</sub>O for 29 days:

5.2%

51

Storage over H<sub>2</sub>SO<sub>4</sub> for 29 days:

4.7%

Two days in oven at 105°C:

4.3%

Solubility Data: Insoluble in water, but soluble in acids, alkalis and ammonia.

1, 29

Zinc, Zn (page 3)

Health Hazard: Zinc powder is slightly to moderately toxic. When heated fumes of ZnO evolve, which when inhaled can cause "brass founder's ague" or "brass chills" and fever, also cause "zinc-fume fever," "zinc chills" or "galvo." The effect is usually temporary.	93, 12, 25, 29
M.A.C. of zinc (as ZnO), mg./m. <sup>3</sup> :	15
Safety Classifications:	
OSM:	class 2
ICC:	not listed
Fire and Explosion Hazard: Powdered zinc when heated is an explosive and fire hazard. It burns with intense heat. Prevent water from contacting the material. Store and process only in buildings or rooms adequately vented at the highest point to prevent the accumulation of evolved hydrogen gas. When compounded with oxidizing agents, the powdered metal is a dangerous fire and explosive hazard. In the repair or maintenance of buildings or equipment, powdered dust should be removed and nonsparking tools used. Fight fire with special mixtures of dry chemicals, or powdered talc.	12, 14, 49, 51
See also Ref. 86	75
Electrostatic Sensitivity (minimum energy required for ignition of powder by electric sparks, millijoules):	(dust cloud) 650
Ignition Temperature, °C:	(dust cloud) 20
	(dust layer) 100
Minimum Explosive Concentration, mg./l.:	425
Use in Pyrotechnics: As a fuel. On burning, it produces a white light with a bluish-green or bluish tint.	20, 29

# ZINC CARBONATE

ZINC CARBONATE				Refs.
Formula:	ZnCO <sub>3</sub>			
Specification No.:	MIL-Z-12061			
Molecular Weight:	125.39			
Crystalline Form:	trigonal			1
Color:	white			29
	colorless			1
Density, g./ml.:	(solid) 4.44			1
Coefficient of Thermal Expansion:	-----			
Heat of Formation, Kcal./mole at 298°K.:	(c) -194.2			9
Free Energy of Formation, Kcal./mole at 298°K.:	(c) -174.8			9
Entropy, cal./deg./mole at 298°K.:	19.7			3, 9
Melting Point:	loses CO <sub>2</sub> at 573°K (300°C)			1
Heat of Fusion:	-----			
Boiling Point:	-----			
Transition Point:	-----			
Heat of Sublimation:	-----			
Heat Content or Enthalpy:	-----			
Heat Capacity, cal./deg./mole:	(solid) 19.16			9
Molal Heat Capacity can be estimated from $C_p = 9.30 + 33.0 (10^{-3}T)$ at 298-780°K				4
Decomposition Temperature:	loses CO <sub>2</sub> at 300°C			
Commercial ZnCO <sub>3</sub> gives off some CO <sub>2</sub> even at 90°C. Decomposition is complete at 300° in 1 hour, and at 400° in 1/2 hour.				1
Decomposition Products:	ZnO + CO <sub>2</sub>			54V4
Heat of Dissociation, cal./mole:	21,000			54V2
Dissociation Pressure: A constant reproducible decomposition pressure has not been observed. The decomposition depends on the grain size and other factors.				44S32 sup
X-Ray Crystallographic Data:				
System	Space Group	a	Axial Angle	Molecules/ Unit Cell
hexagonal	D <sub>3d</sub> <sup>6</sup>	5.704	α = 48° 6'	2
Hygroscopicity:	-----			1
Solubility Data:				
In water at 15°C:			0.001 g.	1, 12
In acids, alkalies, NH <sub>4</sub> salts:			soluble	
In NH <sub>3</sub> , acetic acid, pyridine:			insoluble	
Health Hazard:	low			

**Zinc Carbonate (page 2)**

**Safety Classifications:**

OSM:

not listed

ICC:

not listed

Fire and Explosion Hazard:

\_\_\_\_\_

Electrostatic Sensitivity:

\_\_\_\_\_

Use in Pyrotechnics:

as a retardant

17



**ZINC OXIDE, ZnO**  
(Chinese White, Zinc White, Flowers of Zinc,  
Zinc Bloom, Philosopher's Wool)

		<i>Refs.</i> 1, 11, 29
Specification No.:	MIL-Z-291B	
The specification covers three grades of which grades 1 and 2 are used in pyrotechnic mixtures. They differ somewhat in purity (grade 2 is the purer) and have the same granulation.		
Molecular Weight:	81.38	
Crystalline Form:	amorphous powder	1
Color:	white (or yellowish)	1
	Becomes lemon yellow on heating, regaining its white color on cooling.	52V11
Density, g./ml.:	(solid) 5.47	1
Coefficient of Thermal Expansion, cubical:	(aver.) $1.8 \times 10^{-7}$	31
Heat of Formation, Kcal./mole at 298°K:	(fused) -84.35 (c) -83.17	1, 9
See Table a		
Free Energy of Formation, Kcal./mole at 298°K:	(c) -76.05	1, 9
See Table a		
a. HEAT AND FREE ENERGY OF FORMATION OF ZnO (c)		2

T, °K	$\Delta H$ (cal./mole)	$\Delta F^\circ$ (cal./mole)
298.16 . . . .	-83,250 ( $\pm 200$ )	-76,100 ( $\pm 200$ )
400 . . . . .	-83,150	-73,650
500 . . . . .	-83,050	-71,300
600 . . . . .	-82,950	-68,950
692.7 . . . .	-82,850	-66,800
692.7 . . . .	-84,600	-66,800
700 . . . . .	-84,600	-66,600
800 . . . . .	-84,550	-64,050
900 . . . . .	-84,500	-61,450
1000 . . . . .	-84,400	-58,900
1100 . . . . .	-84,300	-56,350
1180 . . . . .	-84,200	-54,350
1180 . . . . .	-111,600	-54,350
1200 . . . . .	-111,550	-53,350
1300 . . . . .	-111,150	-48,500
1400 . . . . .	-110,750	-43,700
1500 . . . . .	-110,350	-38,950
1600 . . . . .	-109,900	-34,200
1700 . . . . .	-109,450	-29,500
1800 . . . . .	-109,000	-24,800
1900 . . . . .	-108,550	-20,150
2000 . . . . .	-108,100	-15,500

Zinc Oxide, ZnO (page 2)

Phase Changes of Metal  
M.P., 692.7°K;  $\Delta H = 1765$  cal./g.-atom  
B.P., 1180°K;  $\Delta H = 27,430$  cal./g.-atom

Free Energy Equations:

Reactions	Range of Validity, °K
1) $\text{Zn (c)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{ZnO (c)}$	298.16-692.7
$\Delta F^\circ = -84,670 - 6.40 (T \log T) + .84 (10^{-5} T^2) + .99 (10^5 T^{-1}) + 43.25 T$	
2) $\text{Zn (l)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{ZnO (c)}$	692.7-1180
$\Delta F^\circ = -85,520 - 1.45 (T \log T) - .36 (10^{-5} T^2) + .99 (10^5 T^{-1}) + 31.25 T$	
3) $\text{Zn (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{ZnO (c)}$	1180-2000
$\Delta F^\circ = -115,940 - 7.28 (T \log T) - .36 (10^{-5} T^2) + .99 + (10^5 T^{-1}) + 74.94 T$	

Entropy, cal./deg./mole at 298°K:

See Tables b, c

Melting Point:

> 2073°K (> 1800°C)  
zincite, 2243°K (1975°C)  
4470

Heat of Fusion, g./cal./mole:

Boiling Point:

decomposes  
zincite, decomposes  
2223°K (1950°C)

Transition Point:

Sublimation Temperature:

2073°K (1800°C)

Heat of Sublimation, Kcal./mole:

111-112.5

b. HEAT CONTENT AND ENTROPY OF ZnO (c)  
(Base, crystals at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	1070	3.08	1300	12,120	17.29
500	2190	5.58	1400	13,450	18.28
600	3350	7.69	1500	14,800	19.21
700	4530	9.51	1600	16,160	20.09
800	5740	11.13	1700	17,530	20.92
900	6970	12.57	1800	18,910	21.71
1000	8220	13.89	1900	20,300	22.46
1100	9500	15.11	2000	21,700	23.18
1200	10,800	16.24			

ZnO (c):

Enthalpy:  $H_T - H_{298.15} = 11.71T + 0.61 \times 10^{-5} T^2 + 2.18 \times 10^5 T^{-1} - 4277$   
(0.4 percent; 298-2000°K)

Heat Capacity:  $C_p = 11.71 + 1.22 \times 10^{-5} T - 2.18 \times 10^5 T^{-2}$

## Zinc Oxide, ZnO (page 3)

c. HEAT CONTENT AND ENTROPY OF ZnO (g)  
(Base, ideal gas at 298.15°K)

4

T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole	T, °K	H <sub>T</sub> - H <sub>298.15</sub> cal./mole	S <sub>T</sub> - S <sub>298.15</sub> cal./deg. mole
400 . . . . .	795	2.28	1000 . . . . .	5875	9.99
500 . . . . .	1605	4.10	1200 . . . . .	7630	11.59
600 . . . . .	2435	5.61	1400 . . . . .	9390	12.95
700 . . . . .	3285	6.92	1600 . . . . .	11,160	14.13
800 . . . . .	4140	8.06	1800 . . . . .	12,930	15.17
900 . . . . .	5005	9.08	2000 . . . . .	14,710	16.11

## ZnO (g):

Enthalpy:  $H_T - H_{298.15} = 8.40T + 0.17 \times 10^{-5}T^2 + 0.82 \times 10^5T^{-1} - 2795$   
(0.3 percent; 298-2000°K)

Heat Capacity:  $C_p = 8.40 + 0.34 \times 10^{-5}T^2 - 0.82 \times 10^5T^{-2}$

Heat Capacity, cal./deg./mole at 298°K: (solid) 9.62

9

Temp, °K	20	30	50	100	150	200	300	500	700	900
C <sub>p</sub>	0.17	0.60	1.98	4.24	6.22	7.20	9.66	11.2	11.8	12.3

44S32 sup

Also see equations above

Decomposition Temperature, °K: 2250 ± 25

8

Heat of Decomposition [to Zn(g) and O(g)]

Kcal./mole: < 92

44S32 sup

Decomposition Products: to Zn + O (1673-1748°K)

Addnl. Ref. 3

Vapor Pressure:

Approx. Press. mm.	0.1	1.2	3.5	12	760
Temp. °C	1000	1400	1450	1500	1700

Addnl. Ref. 1

For Dissociation Pressure vs. Temp. see Ref. 54V4 and 44V32 sup

## X-Ray Crystallographic Data:

System	Space Group	a	c	Molecules/Unit Cell
hexagonal	C <sub>6v</sub>	3.24265	5.1948	2

1

Hygroscopicity: Absorbs H<sub>2</sub>O and CO<sub>2</sub> from air. The rate of absorption is greater the finer the oxide and increases with rising temp.

44S32 sup

Solubility Data: In water: .00016 g./100 ml. at 29°C

In mineral acids, dilute acetic acid, NH<sub>4</sub>OH: soluble

1

Health Hazard: Slight to moderately toxic. Zinc oxide is relatively inert, and virtually harmless except when freshly formed. It is an eye irritant, however, and should not be allowed to come into contact with the eyes. Fresh fumes of zinc oxide can cause "brassfounders' ague" or "brass chills," etc.  
(See Zinc.)

93

25

29

M.A.C. mg./m.<sup>3</sup> of air for an 8 hr. working day: 15

14

**Zinc Oxide, ZnO (page 4)**

**Safety Classifications:**

OSM:	not listed
ICC:	not listed

Fire and Explosion Hazard:	none listed
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**Precautions When Handling:**

Handle carefully to avoid excessive "dusting." Keep work area clean, and wash hands frequently.

Store in sealed containers away from acids.

If it enters the eye, thorough washing of the eye in a bubble type fountain or inverted faucet will remove the irritating particles. Take the victim to a physician immediately for examination and further treatment.

**Electrostatic Sensitivity:**

Use in Pyrotechnics: A product of the burning or oxidation of zinc. Used in screening smoke compositions.

**Additional References:**

- 1) "Zinc Oxide Rediscovered," H. E. Brown, New Jersey Zinc Company, New York
- 2) Pol. 64
- 3) "The Stability of Gaseous Diatomic Oxides," Brewer and Mastie, J. Chem. Phys., 19, 834 (1951)

# ZINC STEARATE

Refs.

Formula:  $\text{Zn}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$   
 Specification No.: \_\_\_\_\_  
 Molecular Weight: 632.30  
 Crystalline Form: Light powder, talc-like to touch, usually marketed as a fine powder about 300-325 mesh.  
 Color: white  
 Density: \_\_\_\_\_  
 Coefficient of Thermal Expansion: \_\_\_\_\_  
 Heat of Formation: \_\_\_\_\_  
 Free Energy of Formation: \_\_\_\_\_  
 Entropy: \_\_\_\_\_  
 Melting Point: 403°K (130°C)  
 Melts to a clear water-white liquid and cools to a translucent glassy mass of crystalline appearance and which is easily powdered.  
 Heat of Fusion: \_\_\_\_\_  
 Boiling Point: \_\_\_\_\_  
 Transition Point: \_\_\_\_\_  
 Heat of Sublimation: \_\_\_\_\_  
 Heat Content or Enthalpy: \_\_\_\_\_  
 Heat Capacity: \_\_\_\_\_  
 Decomposition Temperature: \_\_\_\_\_  
 Decomposition Products: \_\_\_\_\_  
 Vapor Pressure: \_\_\_\_\_  
 X-Ray Crystallographic Data: \_\_\_\_\_  
 Hygroscopicity: nonhygroscopic (repels water)  
 Solubility Data:  
 In water, alcohol, ether: insoluble  
 In benzene: soluble

16, Addnl.  
Ref. 1

1  
Addnl. Ref. 1

29

1

Addnl. Ref. 1

Temp. °C	CH <sub>3</sub> OH	Toluol
25	0.04*	0.04*
50	0.06	0.27
75	1.88	1.98
100	6.56	4.97

\*g. of stearate/100 g. solvent.

For additional solubility data see Addnl. Ref. 3

Health Hazard: low  
 Inhalation of the powder can lead to pulmonary inflammation.

12, 29

Safety Classifications:

OSM: not listed  
 ICC: not listed

**Zinc Stearate (page 2)**

**Fire and Explosion Hazard:**

Autoignition Temp., °F:

790

15, 71

Flash Point (open cup), °F:

530

Electrostatic Sensitivity:

Use in Pyrotechnics:

as a retardant, fuel,  
and binder

17

**Additional References:**

- 1) "Metallic Soaps—Their Uses, Preparation and Properties," W. F. Whitmore and M. Lauro, Ind. Eng. Chem., 22, 646 (1930)
- 2) "Aero Metallic Stearates," (pamphlet) American Cyanamid Co. (1960)
- 3) "The Solubility of Zinc Soaps in Organic Solvents," E. P. Martin and R.C. Pink, J. Chem. Soc. 1750 (1948)

## ZIRCONIUM, Zr

Refs.

Specification No.:

PAPD-464

Specification PAPD-464 covers two classes which differ in purity. A type of zirconium powder has been developed which is made by a new process, and has three granulations A, B, and C. This new type is covered by new specification FA-PD-MI-2364. Granulations A and B of this type are packed, shipped, and handled dry. Granulation C of this type is packed, shipped, and stored under water.

Molecular Weight:

91.22

Crystalline Form:

cubic

Color: The bulk metal is silvery white to grey. Dry colloidal Zr and finely pulverized Zr are black and resemble carbon in appearance. Coarser granulations are steel-grey in color and look like crushed cast iron.

Density, g./ml.:

(solid) 6.49

Coefficient of Thermal Expansion, linear:

hexagonal,  $\alpha$  form (298–1143°K)—linear

along  $a$  axis:

$5.5 \times 10^{-6}$

along  $c$  axis:

$10.8 \times 10^{-6}$

cubic,  $\beta$  (1143–1600°K):

$9.7 \times 10^{-6}$

Range °C

Coeff. (linear)

–183 to 0

$4.6-5.1 \times 10^{-6}$

0–20

$4.6-5.9 \times 10^{-6}$

20–200

$5.4 \times 10^{-6}$

20–400

$6.1 \times 10^{-6}$

20–700

$7.1 \times 10^{-6}$

Heat of Formation, Kcal./mole at 298°K:

(gas) 125

Free Energy of Formation, Kcal./mole at 298°K:

(gas) 115

Entropy, cal./deg./gm. at 298°K:

(c) 9.29

(gas) 43.31

See Tables a and b

Melting Point:

2125°K (1832°C)

Heat of Fusion, cal./mole:

4000

Boiling Point:

4650°K (4377°C)

Ref. 39 gives 3577°C (3850°K). Other refs. vary appreciably.

Heat of Vaporization, cal./mole:

139,000

Transition Point, °K:

1135

Heat of Transition, cal./mole:

920

Heat of Sublimation, cal./mole:

146,000

Heat Content or Enthalpy, cal./mole at 298°K:

(solid) 1313

See equations below

a. HEAT CONTENT AND ENTROPY OF Zr (c, l)  
(Base, crystals at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	650	1.87	1600	10,680	12.98
500	1330	3.39	1700	11,470	13.46
600	2030	4.66	1800	12,260	13.91
700	2740	5.76	1900	13,050	14.33
800	3460	6.72	2000	13,840	14.74
900	4200	7.59	2100	14,630	15.12
1000	4980	8.41	2130 (c)	14,870	15.24
1100	5800	9.20	2130 (l)	19,770	17.54
1135 (α)	6090	9.46	2200	20,330	17.80
1135 (β)	7005	10.26	2400	21,930	18.49
1200	7520	10.70	2600	23,530	19.13
1300	8310	11.33	2800	25,130	19.72
1400	9100	11.92	3000	26,730	20.28
1500	9890	12.47			

## Zr (α) :

Enthalpy:  $H_T - H_{298.15} = 6.50T + 0.71 \times 10^{-5}T^2 + 0.82 \times 10^5T^{-1} - 2276$   
(0.7 percent; 298-1135°K)

Heat Capacity:  $C_p = 6.50 + 1.42 \times 10^{-5}T - 0.82 \times 10^5T^{-2}$

## Zr (β) :

Enthalpy:  $H_T - H_{298.15} = 7.90T - 1960$  (0.1 percent; 1135-2130°K)

$\Delta H_{2130}$  (fusion) = 4900

## Zr (l) :

Enthalpy:  $H_T - H_{298.15} = 8.00T + 2730$  (0.1 percent; 2130-3000°K)

b. HEAT CONTENT AND ENTROPY OF Zr (g)  
(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	665	1.92	1900	10,325	11.92
500	1325	3.39	2000	11,025	12.28
600	1980	4.58	2200	12,450	12.96
700	2620	5.57	2400	13,905	13.59
800	3245	6.40	2600	15,390	14.18
900	3870	7.13	2800	16,900	14.74
1000	4475	7.78	3000	18,435	15.27
1100	5085	8.36	3500	22,410	16.50
1200	5705	8.90	4000	26,575	17.61
1300	6335	9.40	4500	30,925	18.63
1400	6970	9.87	5000	35,430	19.58
1500	7620	10.32	6000	44,750	21.28
1600	8280	10.75	7000	54,235	22.74
1700	8950	11.15	8000	63,645	24.00
1800	9530	11.54			



Zirconium, Zr (page 3)

Zr (g) :

Enthalpy:  $H_T - H_{298.15} = 7.01T - 0.35 \times 10^{-3}T^2 + 0.38 \times 10^5T^{-1} - 2186$   
(0.7 percent; 298-1400°K)

Heat Capacity:  $C_p = 7.01 - 0.70 \times 10^{-3}T - 0.38 \times 10^5T^{-2}$

Enthalpy:  $H_T - H_{298.15} = 5.59T + 0.36 \times 10^{-3}T^2 - 0.50 \times 10^5T^{-1} - 1531$   
(0.3 percent; 1400-6000°K)

Heat Capacity:  $C_p = 5.59 + 0.72 \times 10^{-3}T + 0.50 \times 10^5T^{-2}$

Heat Capacity, cal./deg./mole at 298°K: (liquid) 8.00  
( $\alpha$  form) 6.01  
( $\beta$  form) 7.90

4, 5

c. HEAT CAPACITY OF Zr

(Solid I, 298-1143°K; Solid II, 1143-2125°K;  
Liquid, 2125-3000°K)

T, °K	$C_p^\circ$ (cal./deg./mole)
298	6.01
400	6.36
600	6.88
800	7.34
1000	7.79
1100	8.01
1200	6.79
1600	7.43
2000	8.07
2100	8.23
2200	
to	
3000	8.00

See also equations above

Decomposition Temperature: —

Decomposition Products: —

Vapor Pressure: For 1949-2054°K the following equation holds:

$\log P$  (atm.) =  $-31,066/T + 7.3351 - 2415 \times 10^{-4}$  (where T = absolute temp.)

39

Press. atm.	$10^{-4}$	$10^{-3}$	$10^{-2}$	1
Temp. °K	2450	2700	3000	3850

X-Ray Crystallographic Data:

System	Space Group	a	c	Molecules/Unit Cell
hexagonal	$D_{6h}^{14}$	3.223	5.123	2
cubic	$O_h$	3.61		

1

28

Hygroscopicity: —

Solubility Data: Insoluble in water. Soluble in HF, aqua regia, hot phosphoric acid. Slightly soluble in acids.

1

## Zirconium, Zr (page 4)

### Safety Classifications:

OSM: (dust) class 1  
ICC: flammable solid;  
yellow label

**Fire and Explosion Hazard:** Dry Zr powder or sponge is a pyrophoric solid liable to spontaneous combustion and burns in air with intense heat. It may explode particularly in the presence of water due to evolution of hydrogen. The explosive range of dust clouds of Zr powder in air is about 45 to 300 mg./l. The range of fire and explosion is increased by heat and the presence of oxidizers.

12, 14, 15,  
26, 28

**Caution:** Do not use water to fight fire. Use special mixtures of dry chemical salt, dry sand, or powdered talc. Use only nonsparking tools for repair or maintenance in storage areas.

49, 51, 75

**Health Hazard:** Zirconium powder is believed to be nontoxic. Zirconium and its alloys explode when treated with nitric acid.

93

M.A.C., mg./m.<sup>3</sup>: 5

12

### Precautions When Handling:

Zirconium powder (PAPD) is shipped and stored wet. In no case should it be shipped and stored in anything larger than a one-gallon can, nor should the moisture content be reduced to less than 25 percent by volume. Powder containing 5-15% water is extremely dangerous. When once ignited, it burns even more violently than the dry powder. All operations with the powdered metal must be performed in an inert atmosphere, and persons working with it require protective clothing including gloves and face protection. Waste zirconium powder, rags, and other materials that have come in contact with it must be segregated from other wastes, immersed in water, and disposed of at once. At ordinary temperature Zr is not very reactive as a thin protective coating of oxide on the surface is formed.

28

Zr readily combines with oxygen and the rate is appreciable at 200°C. The energy of activation of the reaction has been determined as 18.2 Kcal./mole and the entropy of activation as -25.6 cal./mole.

Zr combines not only with oxygen, but also with nitrogen, carbon, and silicon.

16

At high temperatures Zr burns with a brilliant white light. When the hot metal is treated with steam at 700-800°C, free hydrogen is evolved.

39

**Autoignition Temperature:** 500°F

75

See FA-PD-M I-2364 for handling the new type of Zr.

**Electrostatic Sensitivity** (minimum energy required for ignition of powder by electric sparks, millijoules):

26

(dust cloud) 5  
(dust layer) 0.001

**Use in Pyrotechnics:** As a fuel, and a component of nongaseous fuze powders.

17

### Additional References:

- 1) "The Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium, and Their Hydrides," I. Hartmann et al., Bureau of Mines, RI4835 (Dec. 1951)
- 2) "Metallurgy of Zirconium," B. Lustman and F. Kerze, Jr., McGraw-Hill Book Company, New York (1955) for data on the various physical properties of Zr.

## ZIRCONIUM HYDRIDE, $ZrH_2$ (not a definite chemical)

Zirconium readily absorbs hydrogen even at room temperature, forming brittle, metallic-like materials whose compositions vary with the amount of hydrogen absorbed and approach  $ZrH_2$  as the limiting maximum hydrogen content. The absorption is reversible and at constant pressure decreases with increasing temperature. The optimum temperature for absorption of H by Zr is given as 300°C. However, the data of Addnl. Ref. 4 show a higher absorption at 20° and 150°C, i.e., 24,000 cc. at S.T.P. per 100 g. of metal and 23,700 cc. at 300°C. The absorption of H by Zr is exothermic and results in a large increase in volume, approximately 15%. The absorbed  $H_2$  is completely liberated at about 800°C. Absorption depends to some extent on the surface condition of the Zr.

Zirconium hydrides have been prepared by

- 1) Heating the prepared metal with  $H_2$ .
- 2) Forming the metal in the presence of  $H_2$ .
- 3) Treating  $ZrO_2$  with  $CaH_2$  at 500–1000° in an atmosphere of  $H_2$ .

Although Zr and  $H_2$  do not form definite compounds, five well-defined crystal phases of the two are recognized. These have been designated  $\alpha$ ,  $\beta$ , etc. The  $\delta$  phase is a face-centered tetragonal phase which includes the range from  $ZrH_{1.67}$  to close to  $ZrH_2$ , and corresponds to about 66.7 atom % of  $H_2$ .

Specification No.:	MIL-Z-21353	
Molecular Weight:	93.24	
Crystalline Form:	powder	1
Color:	dark grey to black	1, 29
Density, g./ml.:	(solid) 5.6 5.74	12 50V15
Coefficient of Thermal Expansion:	—	
Heat of Formation for $ZrH_{1.00}$ , Kcal./mole:	38.9	50V15
Free Energy of Formation:	—	
Entropy:	—	
Melting Point:	—	
Heat of Fusion:	—	
Boiling Point:	—	
Transition Point:	—	
Heat of Sublimation:	—	
Heat Content or Enthalpy:	—	
Heat Capacity:	—	
Decomposition Temperature:	apparent above 100°C	28
Decomposition Products:	hydrogen driven off	
Vapor Pressure:	—	

Refs.

28, 39, Addnl.  
Ref. 1

# Zirconium Hydride, ZrH<sub>2</sub> (page 2)

## X-Ray Crystallographic Data (for a hydrogen content approaching ZrH<sub>2</sub>) :

System	Space Group	a	c	Molecules/ Unit Cell	
tetragonal		4.364	4.440		28
tetragonal (ε phase)		3.513	4.450	4	Addnl. Ref. 3 44S42
Hygroscopicity:		—			
Solubility Data:		—			
Health Hazard:		—			
Safety Classifications:		—			
OSM:			not listed		
ICC:			not listed		
Fire and Explosion Hazard: Dangerous, due to evolution of hydrogen. At higher temperatures ZrH <sub>2</sub> reacts with oxygen and with oxygen containing compounds. It may ignite and explode with water.					12, 39
See also Ref. 44V42					
Electrostatic Sensitivity (minimum energy required for ignition of powder by electric sparks, millijoules) :			(dust cloud) 60 (dust layer) .064		26
Activation Energy, at 1 atm., cal./mole:			17,200 ± 200		17
Use in Pyrotechnics:			in igniting flares and as a fuel		
Minimum Explosive Concentration of Zirconium Hydride Powder, mg./l.:					26
See Also Addnl. Ref. 1			85		
Autoignition Temperature, 300–600°C:			(dust cloud) 350 (dust layer) 270		28, 26
Additional References:					
1) T. B. Douglas and A. C. Victor, J. Research N.B.S. 61, 13 (1958)					
2) "The Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium and Their Hydrides," I. Hartmann et al., Bureau of Mines, RI 4835 (1951)					
3) "The Crystal Structures of ThH <sub>2</sub> and ZrH <sub>2</sub> ," R. Rundle et al., Z. Phys. Chem. 11B, 433 (1931)					
4) Hall et al., Tran. Far. Soc. 41, 306 (1945) cited in Ref. 40					

## ZIRCONIUM-NICKEL ALLOY (Powdered)

*Refs.*

Formula:	(Spec.) Zr/N: 70/30 and 30/70
Specification No.:	MIL-Z-11410A
The specification covers two types. Type I is a 70/30 and Type II a 30/70 Zr/Ni alloy.	
Molecular Weight:	—
Crystalline Form:	cubic
Color:	silver white to grey
Density, g./ml.:	(solid) 6.4
Coefficient of Thermal Expansion:	—
Heat of Formation:	—
Free Energy of Formation:	—
Entropy:	—
Melting Point:	—
Heat of Fusion:	—
Boiling Point:	—
Transition Point:	—
Heat of Sublimation:	—
Heat Content or Enthalpy:	—
Heat Capacity:	—
Decomposition Temperature:	—
Decomposition Products:	—
Vapor Pressure:	—
X-Ray Crystallographic Data:	—
Hygroscopicity:	—
Solubility Data:	resistant to acids and alkalies
Health Hazard:	—
Safety Classifications:	
OSM:	(dust) class 2
ICC:	not listed
Fire and Explosion Hazard: The specification requires that the alloy be packed in heat sealed inert plastic liners, such as polyethylene, in new clean metal containers.	
Electrostatic Sensitivity:	—
Use in Pyrotechnics:	as a fuel; a vigorous deoxidizer

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### Additional References:

- 1) For the Zr-Ni system up to 40% Ni see E. T. Hayes et al., "The Zirconium-nickel diagram," *Trans. Amer. Soc. Metals*, 45, 893 (1953)